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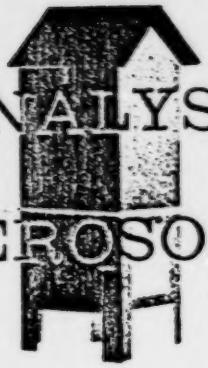

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16. ABSTRACT

Sampling and analysis requirements for the characterization of ambient particles are reviewed. The choice of sampling equipment and characterization procedures for ambient particles are often dictated by the objectives of the experiment. The paper describes the procedures and the application of the following instrumental methods for the characterization of aerosols: x-ray fluorescence (XRF), neutron activation (NAA), inon exchange chromatography (IC), x-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy (SEM). A procedure for the application of gas phase denuders to measure nitric acid and nitrates and a combustion procedure to measure the carbon content of particles are also described.

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Sampling and Analysis of Ambient Aerosols

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Introduction

The atmosphere is an enormously complex, more or less effective, mixing vessel. And yet, in spite of that complexity (numerous sources, sinks, transport processes, and transformations), the aerosol particles found there retain distinctive distributions with respect to size and composition. The bimodal size distribution for aerosols* has been found in various regions by many investigators, and analysis of the particle size fractions has shown that the two modes differ considerably in their elemental constituents and in their chemistry. For example, the fine particle fraction is often acidic; and the coarse particle fraction, is often basic. This interesting dichotomy is consistent with the view that the fine particle fraction is constituted largely of particles formed and accreted from atmospheric gases, and that among these gases are the acidic oxides of sulfur and nitrogen.** On the other hand, the coarse particle fraction is mainly formed from the larger particles breaking up, among which are metals (Ca, K), the oxides of which are basic. These properties of atmospheric particles are schematically represented in Figure 1.

In general, we find that the elements sulfur and lead appear mostly in the fine fraction, and calcium, aluminum, and silicon appear mostly in the

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* Aerosol particles will be referred to as "aerosols", not to be confused with gas and solids or liquids.

** The relative contribution of nitrogen oxides to particle formation is now a controversial subject, and evidence exists that previous estimates were considerably too high.

coarse fraction. These elements, which usually appear in quantities measured in micrograms per cubic meter, are not thought of as trace elements.

In practice, our primary interest in measuring materials in the atmosphere is to provide information for pollution control. Two complementary orientations to this problem exist. In "source apportionment models," one begins with the measurements of elemental abundances in particles collected downwind of the sources and works back through a model to determine the contribution of the sources to particulate mass loading. In "air quality simulation models," one takes a continuity (conservation) equation describing material in the atmosphere, and various input and output data (source emission rates, meteorological parameters, rates of transport and transformation, etc.) and calculates the air quality. The test of the model calculation is the agreement of its predicted values with experimental observations of air quality. Experimental determinations of elements in atmospheric particles are necessary, then, in both approaches to the assignment of atmospheric sources: one approach works from the observations back to the source, and the other work from the source to the observations. These remarks are illustrated in Figure 2.

The following sections of the paper discuss the requirements for the collection and analysis of ambient particles to determine the mass and elemental composition and to determine the physical properties and chemical species present in the sample. The choice of sampling equipment and characterization procedures for ambient particles for environmental study data collection should be dictated by the objectives of the study. In the case of determining the effects of aerosols on surfaces, the identification and the physical and chemical properties of as many of the components that constitute the aerosol sample should be an integral part of the study.

The discussion that follows also describes the procedures and the application of the following instrumental methods for particle characterization: X-ray fluorescence (XRF), neutron activation (NAA), ion exchange chromatography (IC), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM). Also, the procedure for and application of gas phase denuders to measure HNO_3 and nitrate, and a combustion method to measure the carbon content of particles will be described.

From this array of analytical procedures, the chemical and physical properties of ambient particles are determined and their potential effects impact on man and materials can be inferred. In addition, the sources of the ambient particles can be identified from these same chemical properties, e.g., elemental composition is used as input to receptor models (1). Some examples of receptor modeling are also presented later in this report.

SAMPLERS AND FILTER MEDIA

Today there are many aerosol sampling methods; unfortunately, no one particle collection method will be acceptable for the range of measurements necessary for the comprehensive chemical analysis that would be required in many air quality environmental impact studies. For the purpose of this presentation, we assume particle sample collection will be made over 24 hour periods and that particles <2.5 μm in diameter (fine fraction) and the particles > 2.5 μm in diameter (coarse fraction) are of interest and will be collected and analyzed. In addition, we will assume the need to measure chemical and physical properties of each of these fractions. Also, the samples are to be analyzed for both inorganic and organic content.

Dichotomous Sampler: One particle collection system that has been used frequently by the U.S. Environmental Protection Agency (EPA) to provide samples compatible with the above discussed requirements is the dichotomous sampler. This sampler is designed to use either Teflon or quartz filters that satisfy another important requirement in aerosol characterization studies: the sample collection will be nearly free from artifact formation. Table 1 contains a list of types and chemical properties of filters that are widely used in air pollution monitoring studies. Note the alkalinity of the glass fiber filters, responsible for sulfate artifacts during sampling.

Table 1. Properties of filters used to colllect ambient particulate samples.

SUMMARY OF USEFUL FILTER PROPERTIES

FILTER AND FILTER COMPOSITION	DENSITY mg/cm^2	pH	FILTER EFFICIENCY %*
TEFLON (MEMBRANE) $(CF_2)_n$ (2μm PORE SIZE)	0.5	NEUTRAL	99.95
CELLULOSE (WHATMAN 41) $(C_6H_{10}O_5)_n$	8.7	NEUTRAL (REACTS WITH HNO_3)	58% AT 0.3 μm
GLASS FIBER (WHATMAN GF/C)	5.16	BASIC pH - 9	99.0
"QUARTZ" GELMAN MICRO—QUARTZ	6.51	pH - 7	98.5
POLYCARBONATE (NUCLEPORE) $C_{15}H_{14} + CO_3$ (0.3μmPORE SIZE)	0.8	NEUTRAL	93.9
CELLULOSE ACETATE/NITRATE MILLIPORE (1.2μm PORE SIZE) $(C_9H_{13}O_7)_n$	5.0	NEUTRAL (REACTS WITH HNO_3)	99.6

*MINIMUM EFFICIENCY FOR PARTICULATE DIAMETER >0.035μm AT V = 10cm/sec

Sampling artifacts are defined as the chemical reactions of acidic gases with certain types of filters to form nonvolatile species, e.g., $SO_2 + M \rightarrow SO_4M$ or $HNO_3 + M \rightarrow MNO_3$; where M is a metal impurity (e.g., Na, Ca) in the collection substrate. Thus, the true sulfate and nitrate concentration is perturbed by this artifact. Glass fiber filters and cellulose membrane filters are notorious for producing sulfate and nitrate artifacts (2).

The dichotomous sampler is a virtual impactor that aerodynamically separates particles into size fractions corresponding to the fine and coarse modes of the normal size distribution of ambient particles and deposits the particles uniformly on the filters. A schematic diagram of the dichotomous sampler is shown in Figure 3. More detailed diagram of the inertial impactor separation stage is shown in Figure 4. Ambient particles should be collected on 1 or 2 μm pore size Teflon filter (Membrana Corp., Pleasanton, CA) if the elemental composition is to be determined accurately by XRF or ionic content. (3). Teflon filters are the filter medium of choice because they are inert, chemically pure, and have a high collection efficiency, as noted in Table 1. The density of 2 μm pore size membrane Teflon filter is approximately 500 $\mu g/cm^2$. This low density is ideal for XRF and mass measurements while having > 99% collection efficiency for particles > 0.05 μm in aerodynamic diameters. However, quartz filters are used for condensable carbon measurements in field studies because total condensable carbon content is typically measured by a thermal combustion procedure described by Huntzicker et al. (4). This combustion procedure will be discussed in detail in the measurement section of this report.

Cyclone Samplers: In field studies where only the fine particles (<2.5 μm) are to be collected, cyclone inlets can be used to remove the coarse particles. Figure 5 is an example of a typical sampling system that uses a cyclone inlet, pneumatic flow controller, pump, and filter and particle collection assembly. This aerosol collection arrangement samples the air and deposits the fine particles onto a 37 mm diameter filter. One of the advantages of using cyclone inlets when collecting particles is that a variety of sample flow rates and cutpoints can be used by selecting the appropriate cyclone design. John and Reischl (5) have recently described the properties of several cyclones that would be applicable to air pollution monitoring studies.

ANALYSIS

Mass: The mass of the aerosol collected can be measured by gravimetric procedures. Typically, the mass of aerosol collected on a 37 or 47 mm diameter Teflon filter can be determined to within ± 25 μg per filter. Therefore, if 24 m^3 of ambient air is pulled through a filter and the average particle content is 50 $\mu g/m^3$, the mass of particulates collected on the filter can be measured to a precision of ± 2.08%. For some studies performed by the EPA, mass measurements are made by β-ray attenuation using a method characterized by Jaklevic et al. (6) and Courtney et al. (7). The β-ray attenuation and gravimetric procedures can both determine the mass of aerosol collected on Teflon filters to ± 25 μg. Measurements of mass collected on quartz filters are not as accurate because the quartz is extremely fragile and the weight is difficult to obtain in a micro-balance.

Elemental Composition: There are a number of analytical procedures that can be used to measure the elemental content of aerosols. Some of these methods require that the sample be extracted and then analyzed by an emission spectrographic procedure. For example, Scott et al. (8) reported multi-element analysis of about one thousand Hi-vol filters by low temperature oxygen ashing and followed by acid extraction of the filter and analysis of the extract by optical emission spectroscopy (OES). Their paper also provides considerable information on detection limits and confidence levels determined by extensive replicate and standard sample analysis. The absolute sensitivity of OES is not as high as that of some other techniques. The Hi-vol sampler, however, collected so much sample that OES was sufficiently sensitive to provide quantitative determinations of Al, Be, Ca, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Ti, and V in a set of 898 samples from 248 sites in the National Air Surveillance Network (NASN). Determinations were also made of As, Bi, Co, Bs, Sn, Te, and Tl, but the levels were above the detection limit in fewer than 1% of the samples. Table 2 shows the frequency of detection, which is defined as the percentage of samples in which the element is detected at a level above the detection limit. Scott et al. (8) defined the detection limit as the concentration corresponding to a signal three times the standard deviation above the average signal due to the extraction solution. The extraction solution contained internal standards for normalization of measured values.

It is clear from Table 2 that OES analysis of the NASN samples has provided sufficient data to follow trends in abundances of Cu, Fe, Mn, Pb, and Ti, but certainly not As, Bi, Co, Sb, Sn, Te, or Tl, and probably not Mo. Whether sufficient data exist for Al, Be, Ca, Cd, Cr, Mg, Ni, and V depends on more detailed considerations, e.g., comparisons of element levels with

detection limits, interelement interferences, and the requirements of the statistical treatment of the data. Obviously, these results refer only to the 1970 NASN samples; samples from different sites will probably have different frequencies of detection.

Table 2
Frequency of detection by OES of elements in NASN samples.

Number of Samples: 898
Sampling Period: 1970
Sampler and Flow Rate: Hi-vol, 1.7 m^3/min

Element	Frequency of Detection
Cu, Fe, Mn, Pb, Ti	80-100%
Al, Be, Ca, Cd, Cr, Mg, Ni, V	10-80%
Mo	< 10%
As, Bi, Co, Sb, Sn, Te, Tl	< 1%

For many recent air pollution studies, energy dispersive x-ray fluorescence analysis (EDXRF) has been widely used to nondestructively analyze the elemental composition of ambient particles. Stevens et al. (3) used calibration procedures described below to measure the elemental content of ambient particles. The x-ray machine used in these studies was fabricated by Lawrence Berkeley Laboratory and uses a pulsed x-ray tube to excite a secondary target which, in turn, excites the sample with nearly non-energetic x-rays (9).

To obtain high sensitivity for a wide range of elements, each sample is excited by means of three different secondary targets. For the K x-rays of elements with atomic numbers in the ranges 13-20, 21-38, and 39-56, the secondary targets consist of titanium, molybdenum, and samarium, respectively. The molybdenum target also excites the L x-rays of lead and other heavy

elements. The fluorescent x-rays from the sample are detected using a lithium drifted silicon detector, that uses electronic collimation to minimize the background. Because of a compact geometrical arrangement between components of the spectrometer, an x-ray tube power of only 100 W is sufficient to provide the maximum usable count rate for filter samples.

In applications where the amount of collected particulate matter is expected to be small, it is important to estimate the minimum detectable concentration, C'_D. Currie (10) defines C'_D as 3.29 times the standard deviation for determining the background and expresses it as:

$$C'_D = 3.29\eta^{\frac{1}{2}}(St)^{-1}[tR_b + (\Sigma\, t\, R_b)^2]^{\frac{1}{2}} \qquad (1)$$

where: η = measure of extent to which blank is well characterized, S = sensitivity expressed in counts per second per ng cm^{-2} for the spectral region containing the full width at half maximum of the peak for the element of interest, t = counting time in seconds, R_b = background in counts per second for the same spectral region used to determine S for the element, and Σ = relative standard error in determining R_b if errors due to counting statistics were negligible. Assuming that $\Sigma = 0.02$, $\eta = 1$, and t = 100 s for each secondary target, values of C'_D are given in Table 3 for several elements.

To express C'_D in units of ng m^{-3}, one must divide the values in Table 3 by the volume sampled per unit area of filter. For example, this conversion factor is 3.05 m^3 cm^{-2} for 24 h of sampling at a rate of 141 min^{-1} through 6.6 cm^2 of filter area. The corresponding C'_D value for sulfur is 12 ng m^{-3}. If reasonably accurate information on a certain element is needed, then the concentration (C) of that element must exceed C'_D by at least a factor of 3, to insure that C exceeds the standard deviation by a factor of 10. To measure a sulfur concentration of 1 μg m^{-3} for the above example, one could shorten

Table 3. Sensitivities and minimum detectable limits with energy dispersive spectrometer

Element	Secondary target	Sensitivity (Counts per second) (μg^{-1} cm^2)	Background (Rh)	Minimum detectable concentration (C_D) ng cm^{-2}
Al	Ti	7.2	13	203
S	Ti	47	16	36
K	Ti	133	22	16
V	Mo	31	5.8	28
Fe	Mo	67	7.6	15
Se	Mo	199	2.9	3
Sr	Mo	269	6.9	3.6
St	Sm	38	1.7	11.7
Cd	Sm	84	1.8	5.4
Sn	Sm	75	3.5	8.8
Ba	Sm	50	45	74
Pb	Mo	76	3.5	8.6

the sampling time from 24 h to 1 h and still have a sufficient sample for analysis.

After a sample has been irradiated in the EDXRF spectrometer, the resulting spectrum is analyzed to determine the number of counts that each element contributes. To accomplish this, a least-squares procedure is used to find a linear combination of single-element spectra that best describes the unknown spectrum. A library of single-element spectra is obtained for thin standards of each element and is stored in computer memory. The library must contain all elements that could contribute to an unknown sample (3, 9, 10, 11).

The least-squares method is slightly modified for the K x-rays from sulfur to deal with the overlapping M x-rays from lead. Because the concentration of lead can be accurately determined from the emission of L x-rays, it is possible to 'strip' out the interfering lead M peak in the vicinity of the sulfur peak. Such stripping is done prior to performing the least-squares analysis for sulfur. The uncertainty in the result for sulfur

due to the presence of lead is estimated to be about 5% of the lead concentration. For example, if the lead concentration were 2 μg m^{-3}, the resulting sulfur uncertainty would be 0.1 μg m^{-3}. The complete description of the calibration of the EDXRF system is described by Stevens et al. (3).

For most air pollution applications in which only the major elements are needed to determine elemental content of a particulate sample, EDXRF is adequate. However, EDXRF cannot be used to accurately determine elements lighter than Al, or routinely observe the various minute trace elements such as Lu, Hf, Ta, W, Th, Sm, Dy, Yb, Se, As, and La.

A particularly useful combination is EDXRF followed by instrumental neutron activation analysis (INAA). The latter technique, described by Kowalczyk et al. (12) is totally instrumental and, depending on mass loadings and filter blanks, can observe up to 40 elements. Gordon et al. (13) demonstrated the value of applying INAA to samples from the Regional Air Pollution Study that had previously been subjected to XRF. Table 4 is based on their results: these show that the combination of XRF and INAA yielded data for 28 elements in the fine fraction and 32 in the coarse fraction for virtually every sampling period. An additional 18 elements in the fine fraction and 14 in the coarse fraction were observable in about half of the samples. Furthermore, 11 elements (Al, Ca, K, Cl, Ti, V, Mn, Fe, Zn, Br, and Ba) can usually be measured by both methods for a quality assurance check. Thorough INAA requires access to a reactor with a flux of at least 10^{13} n cm^{-2}-s^{-1} and a high-resolution Fe (Li) or intrinsic Ge γ-ray spectrometry system. Irradiations of two different lengths are needed for species of various half-lives (see below).

As presently performed, INAA requires considerably more sample handling and interpretation of results than XRF and, consequently, is considerably more

Table 4. Detectability by XRF and INAA of elements in ambient samples from St. Louis.

Element	Fine fraction		Coarse fraction	
	XRF	INAA	XRF	INAA
Na	Not observable	Strong	Not observable	Strong
Mg	Not observable	Marginal	Not observable	Marginal
Al	Marginal	Strong	Strong	Strong
Si	Strong	Not observable	Strong	Not observable
P	Marginal	Not observable	Marginal	Not observable
S	Strong	Marginal	Strong	Not observable
Cl[a]	Strong	Strong	Strong	Strong
K	Strong	Strong	Strong	Strong
Ca	Strong	Marginal	Strong	Strong
Sc	Not observable	Strong	Not observable	Strong
Ti	Marginal	Marginal	Strong	Strong
V	Marginal	Strong	Marginal	Strong
Cr[a]	Marginal	Strong	Marginal	Strong
Mn	Marginal	Strong	Strong	Strong
Fe	Strong	Strong	Strong	Strong
Co	Not observable	Strong	Not observable	Strong
Ni	Marginal	Not observable	Marginal	Not observable
Cu	Marginal	Marginal	Marginal	Marginal
Zn	Strong	Strong	Strong	Strong
Ga	Marginal	Marginal	Marginal	Marginal
As	Marginal	Strong	Marginal	Strong
Se	Marginal	Strong	Marginal	Strong
Br	Strong	Strong	Strong	Strong
Rb	Marginal	Strong	Marginal	Strong
Sr	Marginal	Marginal	Marginal	Marginal
Mo	Not observable	Marginal	Not observable	Marginal
Ag	Not observable	Marginal	Not observable	Marginal
Cd	Marginal	Strong	Marginal	Marginal
In	Not observable	Marginal	Not observable	Marginal
Sn	Marginal	Not observable	Marginal	Not observable
Sb	Not observable	Strong	Marginal	Strong
I	Not observable	Strong	Not observable	Marginal
Cs	Not observable	Strong	Not observable	Strong
Ba	Marginal	Strong	Strong	Strong
La	Not observable	Strong	Not observable	Strong
Ce	Not observable	Strong	Not observable	Strong
Sm	Not observable	Strong	Not observable	Strong
Tb	Not observable	Marginal	Not observable	Marginal
Dy	Not observable	Marginal	Not observable	Strong
Yb	Not observable	Marginal	Not observable	Marginal
Lu	Not observable	Marginal	Not observable	Strong
Hf	Not observable	Strong	Not observable	Strong
Ta	Not observable	Marginal	Not observable	Strong
W	Not observable	Marginal	Not observable	Strong
Pb	Strong	Not observable	Strong	Not observable
Th	Not observable	Strong	Not observable	Strong

[a]May be unobservable because of filter blank.

costly per sample. Thus, XRF is the preferred screening technique. All samples could be subjected to XRF and the results used to identify only the most interesting samples for further analysis by INAA.

Another way to reduce INAA cost is an approach taken by Watson (14) and Core et al. (15) at the Oregon Graduate Center. Complete INAA requires at least two irradiations of samples: the first for a few minutes to observe species with half-lives of $\leq$15 h, and the second for several hours to observe species with half-lives of up to several years. The former method is less costly to perform, as the γ-ray spectra are simple enough to be resolved primarily by computer. Furthermore, in the former, results are usually available within a day after the irradiation, compared with about three weeks for long irradiations. The Oregon Graduate Center group has employed INAA costeffectively by performing only the short irradiation following XRF analyses. Depending on the conditions, most of the following elements are usually observed: Na, Mg, Al, S, Cl, K, Ca, Ti, V, Mn, Cu, Br, La, Sm, Dy, and W. However, some important elements that are normally observed in long irradiations (Cr, Co, As, Se, and Bs) are usually sacrificed in this approach.

Many other techniques are used to observe elements in atmospheric particulate matter, including atomic absorption spectrophotometry, inductively coupled plasma atomic emission spectrometry, spark-source mass spectrometry, various electrochemical methods (such as anodic stripping voltammetry), and chemical separations followed by colorimetry. Most require considerable labor per sample to obtain accurate results or (unlike EDXRF and INAA) require dissolution of samples prior to analysis. Moreover, any chemical manipulation greatly increases the chance of contamination by trace elements and loss of volatile or insoluble species.

Ionic Species: The major ionic species present in ambient particles are sulfate ($SO_4^=$), nitrates (NO_3^-), hydrogen (H^+), chlorides (Cl^-), bromide (Br^-) and ammonium (NH_4^+). After EDXRF, analysis samples may then be extracted and the anion and cation concentration measured. The extraction process used when analysis of particles collected on Teflon filters is required consists of removing the filter from its holder, loading it into an extraction vessel, filling the vessel with extraction solution, and then extracting by the use of an ultrasonic bath.

The filters are carefully removed from the filter holders and as quickly as possible placed into the extraction solution in order to prevent contamination. For acidity measurements, care must be taken not to breathe on the filters in order to minimize exposure to exhaled ammonia. The filters are placed in the extraction vessel with the back of each filter facing the bottom in order to prevent any material from being inadvertently removed as the filter is inserted into the vessel.

The extraction vessel recommended is a 30-ml Nalgene polypropylene bottle (Nalge, Inc., Rochester, NY) that has been conditioned by soaking in extraction solution for at least 8 h before use. To keep the filter submerged and open during extraction, a fluted Teflon pipe is placed in the vessel so that the fluted end rests on the outer, unloaded edge of the filter.

The volume of extraction solution used depends on the type and number of analyses performed and ranges from 8 to 20 ml. The extraction solution, perchloric acid, is diluted to 5×10^{-5} N with distilled water. The extraction solution is delivered with 0.05% precision to the vessel by an Oxford Laboratories macro set pipet. The vessel is then capped and placed in an ultrasonic bath (Model 8845-60, Cole-Palmer Instrument Co., Chicago, Illinois) for 20 min. The ultrasonic bath tends to produce standing waves

in the water so that regions exist where no agitation takes place. To overcome this problem, the extraction vessel is continuously moved during the extraction period.

The above extraction procedure is used for analysis of $SO_4^{=}$, NO_3^{-}, NH_4^{+} and H^{+}. For the fine and coarse particle fractions, Stevens et al. (3) found the extraction efficiencies for sulfur to be 98 ± 1% and 95 ± 2%, respectively.

For those samples on which a sulfite determination is to be made, the extraction procedure is modified to minimize the conversion of sulfite to sulfate. Stevens et al. (3) demonstrated that carrying out the extraction at room temperature caused complete conversion of sulfite to sulfate. To prevent such conversion, a cold extraction process was developed. In the modified procedure, the water bath was made up of a slurry of ice and water that maintained the temperature of the sample at 0°C during the extraction. With this procedure 90% of the sulfite was preserved.

Hydrogen ion analysis Titrimetry and a Gran's function plot are recommended to determine strong acidity using the procedure of Brosset and Ferm (16). The instrumentation includes an Orion pH meter, a combination electrode, a Gran's function generator, and a Radiometer autoburett ABU 12. The data can be recorded on a 1-mV strip-chart recorder. The Gran's function generator is an antilog amplifier (Model 755, Analog Devices, Norwood, MA).

The acid analysis procedure is as follows: 1) standardization of sodium hydroxide titrant, 2) measurement of the concentration of the acid extraction solution, 3) titration of extract using the 0.001 N NaOH, and 4) data analysis. Steps 1 and 2 are done once for each set of filter extracts or at least once each day. Nitrogen is bubbled through the solution being titrated to remove an interference by CO_2. The ionic strength of the volume being titrated is maintained at 0.02 M by the addition of KCl.

The method has been characterized by performing 50 measurements on sulfuric acid standards that had a range of concentrations. The linear dynamic range was 10^{-6} to 10^{-4} M. The relative standard deviation was 2% and the minimum detectable level was 1 nano-equivalent ml^{-1} (neq m^{-1}).

Ion exchange chromatography: Ion exchange chromatography is a relatively new technique for routine analysis of anions and cations in aqueous extracts of ambient aerosols. Mulik et al. (17) has described the application of a commercial liquid IC (Dionex Model 14, Sunnyvale, CA) to the analysis of water soluble anions. Before injecting a sample into the IC, 5 ml of the aerosol extract is spiked with a 1:1 mixture of 0.003 M $NaHCO_3$ and 0.0005 M Na_2CO_3 to adjust the molar CO_3^{2-} concentration to the range of 10^{-3} to 10^{-5}. This basic mixture is then added to neutralize the minute concentrations of perchloric acid used in the extraction procedure so that the injected solutions are approximately the molar concentration of the eluent used in the chromatograph. Because the instrument calibration curve is not linear, multi-point calibrations are performed over the range of concentrations expected in the samples. The signal from the IC conductivity detector can be processed by a Hewlett Packard 3385A chromatographic control system. Peak areas and retention times are recorded to quantify and identify specific anions.

Typical relative standard deviations for mixtures of sodium nitrate and ammonium aqueous sulfate standards are shown in Table 5. Retention times and relative standard deviations were determined daily. The minimum detectable levels for sulfates and nitrates were 10^{-1} neq ml^{-1} and 5×10^{-2} neq ml^{-1}, respectively. A typical IC chromatogram of an extract of a fine particle sample collected in Philadelphia is shown in Fig. 6. Note the low nitrate concentration as compared to sulfate. For almost all aerosol samples

collected with the dichotomous sampler using Fluoropore filters, nitrate was always a small fraction of the sulfate concentration.

Table 5. Relative standard deviations for IC analysis of nitrate and sulfate standards.

Molarity	Dionex attenuation setting	Standard deviation* $SO_4^=$	Standard deviation* NO_3^-
1×10^{-4}	10	1%	1%
5×10^{-5}	10	0.3%	1%
1×10^{-5}	3	1.6%	1%

* Based on four consecutive injections of 0.4-ml volumes of standard solutions.

Ammonium analysis: The concentration of ammonium ions may be determined with an ion selective NH_3 gas diffusion electrode (Orion Model 95-10). The response is recorded from a Corning-Digital 112 pH meter. Analysis is performed by mixing 7 ml of filter extract and 0.2 ml of 5 N sodium hydroxide in a 20-ml glass beaker. The electrode is immersed into the solution with the tip extending approximately 1 cm into the solution. Readings are made between 2 and 3 min. after immersing the electrode into the extract. When the sample concentration is less than 1×10^{-5} M, equilibration required as long as 5 min. The electrode is calibrated using dilute NH_4Cl standards (10^{-2} to 10^{-6} M). The minimum detectable level is 3 neq ml^{-1}. At concentrations above 10 neq ml^{-1}, the relative standard deviation is typically ± 5%.

Carbon Measurements and Radioisotopic Analysis of $^{14}C/^{12}C$: Stevens et al. (3) have documented the basis for using Teflon filter substrates to obtain mass measurements and perform XRF analyses for elemental composition. However, carbon measurements are not easily obtained from Teflon filters, because the

procedure used most frequently to measure carbon in aerosols is based on high-temperature combustion methods. For this reason, a second fine particle sample must be collected on quartz at the same time the aerosols are being collected on Teflon. Quartz is used as the collection medium because it has a low carbon content, high collection efficiency, and is chemically inert. An aliquot of the quartz filter can be analyzed by a combustion procedure similar to one described by Stevens et al. (18). This procedure measures volatile carbon and elemental carbon from the same sample. Recent comparisons of methods by Cadle et al. (19) to measure elemental, total and volatile carbon content of aerosols indicate that procedures that depend on combustion or pyrolysis to convert the carbon species into methane followed by flame ionization measurement, may produce substantially different results, depending on the conditions for combustion. For example, to convert completely all the aerosol carbon on quartz filters requires a temperature of at least 850°C and the presence of oxygen in the helium carrier gas. Without oxygen, a substantial amount of elemental carbon will not be pyrolyzed and consequently will not be measured.

At the present time, we measure the elemental and condensable carbon present in ambient particulate samples using a modified Dohrmann DC-50 organic analyzer (DC-50). Figure 8 is a diagram depicting the sample introduction, pyrolysis, combustion and detector assemblies. The DC-50 measures the organic carbon (condensable organics) by pyrolyzing the carbonaceous portion of the sample to CO_2 and other pyrolysis products at 650°C in a helium atmosphere reduces the products to methane over a bed of nickel catalyst in an atmosphere of hydrogen, and measures the methane with a flame ionization detector. After the organic analysis, elemental carbon is determined by combustion of the carbonaceous materials remaining on the quartz filter at 850°C in a 2% oxygen,

98% helium atmosphere. Total carbon is considered to be the sum of the organic and elemental analysis. Recently, we have modified the procedure to collect particles on quartz filters in order to minimize the variations in the blanks. The modification reduces the deposit area of the sample from 37 mm to 13 mm, as shown in Figure 8. This focusing of the sample to a 13 mm area reduces the impact of the carbon blank and the area outside the deposit area becomes the blank for that filter. The combination of increased sample per unit area and a blank for each sample should improve the precision of the combustion procedure to determine carbon content of aerosols.

Currie (20) determined the relative amounts of particulate carbon from contemporary and fossil fuel carbon combustion sources by means of data on the $^{14}C/^{12}C$ ratio. The distinction is possible because contemporary carbon contains trace amounts of ^{14}C, but fossil fuel carbon is essentially devoid of ^{14}C. The $^{14}C/^{12}C$ measurements are relatively expensive and only two or three laboratories in the U.S are capable of performing the analysis. In addition, milligram amounts of material are needed to measure $^{14}C/^{12}C$ in ambient particulate samples. Currie (21) is currently working on a new procedure that measures ^{14}C with an accelerator mass spectrometer at the University of Arizona. With this new system, as little as 100 µg carbon may be analyzed.

Normally, $^{14}C/^{12}C$ is measured at National Bureau of Standards (NBS) by heating the quartz or glass fiber filters to distill the condensable organics from the filters; the organics are then converted to CO_2 and the CO_2 is condensed into a glass microcell. The cell is placed into a sealed chamber and the radioactivity is measured with a sensitive proportional counter. Recently, Stevens et al. (22) reported the presence of carbonates, acetate and formate in aqueous extracts of ambient fine particles collected in the Shenandoah Valley of Northern Virginia, U.S.A. Stevens et al. postulated

these species may interfere with ^{14}C measurements, because the carbonate may result from CO_2 adsorption on the quartz filter. Because almost all of the ambient CO_2 is rich in ^{14}C, the bulk ^{14}C analysis described above may be influenced by the CO_2 artifact formed with the quartz filter. For this reason the improved ^{14}C method described by Currie et al. (21) could be modified to eliminate this problem through an additional step of organic extraction of the ambient sample prior to ^{14}C analysis. This extraction step would all but eliminate the interference due to adsorbed gases (CO_2) on the quartz filters because they would be lost during the evaporation of the solvent after the filter extraction. In addition, measurement of the the ^{14}C content of the major classes of condensable organics is now possible and could enhance the range of species used in receptor models. Another possibility for eliminating the artifact influence would be fractional distillation of the organics from the filter, followed by ^{14}C analysis of the individual thermally released organics. We would expect that only the fraction initially eluted from the filter would contain most of the artifactual ^{14}C.

Electron Microscopy: For many aerosol characterization programs elemental composition and/or ionic content is insufficient to determine the chemical and physical properties of ambient aerosols. Either transmission electron microscopy or SEM is in most cases the only tool to study the properties of individual fine particles. A combination of SEM and TEM x-ray analysis (EDX) of the elemental content of particles enhances the characterization. However, EDX cannot measure C, O, and N, and for certain types of particles, e.g., fly ash, elemental composition of the particle provides insufficient information to identify the particle. For this reason, size and shape coupled with elemental composition provides the information to deduce the morphology of the particles.

More complex techniques are often needed to identify particles; most are destructive techniques and include application of microchemical tests and hot-stage electron microscopy for the characterization of micrometer and sub-micrometer particles. Although these techniques have been used successfully with OM, only a few microscopists have extended these techniques to electron microscopes. Mamane (23), Mamane and de Pena (24), and Mamane and Puschel (26) have described the application of these techniques to the analysis of a variety of ambient particle samples. The best examples of these microparticle reaction tests are the SEM/EDX analysis of $BaCl_2$-treated surfaces for sulfates (Figure 9) and nitron ($C_{20}H_{16}N_4$; 4, 5-dihydro-1, 4 diphenyl-3, 5 phenylimino-1, 2, 4 triazol)-treated surfaces for nitrates (Figure 10). The advantages of these techniques are as follows: a) the method detects ions that cannot be seen by EDX (e.g., nitrates); b) they are inexpensive, sensitive, specific and relatively rapid techniques to measure sulfates and nitrates; c) provide information on mixed individual particles, such as a mineral particle coated with a layer of nitrate or a fly ash particle coated with sulfate (Figure 9), that cannot be obtained by other conventional procedures.

With the hot-stage techniques, particles are exposed to a given temperature while being observed by TEM. During the heating decomposition, melting and sublimation take place. Although the information may not positively identify the particle, these methods can be confirmatory, eliminates certain possibilities and, with the use of other techniques, assists in the identification of the particles.

Collection of particles for electron microscopy is completely different from the collection for other bulk analytical techniques (as wet chemistry or XRF). The following are important when collecting the particles: a) collect

into 3 to 4 size classes, b) particles should remain individual particles on the collection substrate (this normally requires that short sampling time be used to collect the submicrometer particles and that long periods be used for the larger particles. (Mamane et al. (26) describe the use of the Casella impactor to collect the appropriate samples for SEM and TEM analysis. Collection periods for submicrometer ambient particles is typically seconds and minutes for micrometer particles. Large particles (>10 μm) may need sampling times of a few hours. These sampling constraints tend to make comparisons between integrated measurements and SEM results difficult. However, these problems can be reduced through careful selection of sampling periods when bulk and particle-by-particle characterization are to be compared.

X-ray Diffraction and Optical Microscopy Much interest in the composition and source identification of atmospheric aerosols has developed over recent years. In most studies prior to the last decade, much of the compositional characteristics of particulates was inferred from wet chemical analyses, bulk-sample XRF analyses, and optical scattering characteristics. Some work with optical polarizing microscopy yielded results for the major components, but only for those particulates at the coarse end of the size distribution.

During the past decade much more effort has been expended toward development of techniques yielding direct compound identification. An example of a quantitative study of this type is found in the report of Bradway and Record (27) in which optical polarizing analysis of mineral particulates trapped on glass fiber (Hi-vol) filters is given for 14 urban areas. In the work of Stevens et al. (3), particulate compositions were deduced from ion equivalents required by stoichiometry of the compounds with ion

chromatography, Thorin spectrophotometry, and x-ray fluorescence being employed as the analytical methods. Although not a direct observational technique, infrared absorption analysis does provide evidence of the presence of certain compounds according to the observed bond frequencies. Work of Adler and Kerr (28) and Moharram and Sowelim (29) provide infrared information on the occurrence of sulfate ions in various sulfate minerals. Some particulate compounds may be identified by morphological characteristics and their composition deduced by single-particle microbeam scanning electron techniques that will be discussed later. Perhaps the most powerful tool for direct compound identification, both from a qualitative and a quantitative standpoint, is XRD. Difficulty in application of this technique to aerosols comes primarily from the low mass coverage of the particulates on the collecting filter media. Nevertheless, good qualitative studies reporting identification of atmospheric aerosols from filters have been completed by Biggins and Harrison (30), Thompson et al. (31), O'Connor and Jaklevic (32), and Brosset et al. (33). Several of these studies included a separation of the particulate mass into size fractions to identify the dominant compounds in each.

During the past five years, the Institute of Atmospheric Sciences' (IAS) Cloud Physics Laboratory at the South Dakota School of Mines, Rapid City, SD, has worked toward the development of a quantitative technique for analysis of particulate matter collected on various filter substrates. The results of these studies have been reported by Davis et al. (34) and Davis and Johnson (35 and 36). The basis for the technique is the reference intensity method combined with direct beam x-ray transmission measurements. These combined techniques allow the simultaneous determination of crystalline components and the major classes of amorphous components present in thin aerosol layers

collected on filter substrates. Analyses may be completed using Teflon, glass fiber, cellulose acetate, quartz, and polycarbonate filter media.

The XRD procedure developed by Davis et al. (37) to measure the quartz content in ambient particles collected on Teflon filters is based on a mass calibration procedure. The basis of this calibration procedure rests on the provision that, for a monodisperse layer on a thin membrane filter, overlap is negligible and matrix absorption can be ignored. For 3 μm radius spheres of 2.65 density (quartz), such particles can accumulate to the extent of 900 μg cm^{-2} before a monodisperse layer is formed on the filter. For these conditions, therefore, a given laboratory instrument under proper quality assurance procedures may maintain the target x-ray flux at a level sufficiently invariant to complete direct mass calibration analyses over an indefinite period of time. A Norelco diffractometer using a copper target raised to 40 kV and 20 mA power was used for these analyses. Samples were mounted on a Norelco high-angle goniometer fitted with a theta compensator, graphite crystal monochronometer, and spinning sample mount. All samples were scanned from 5° 2θ to 40° 2θ to make a semi-quantitative evaluation of other components. The ratio of peak height to reference intensity constant for each observed component provided a visual estimate of relative abundances for the semi-quantitative evaluation. The quartz peak at 26.67° 2θ (hkl = 101) was used as a basis for the quantitative calibration and analysis.

In conjunction with the reference intensity analysis program, a number of quartz samples were analyzed for scattering power (reference intensity constant values): the Tuscarora quartz was selected from this group as representative of quartz in the environment, the reference intensity constant being close to the average of the set of eight samples analyzed. A linear calibration curve was obtained between μg cm^{-2} and integrated intensity at the

26.67° quartz peak based on a total of 12 calibration analysis completed by loading Teflon filters with a specified weight of fine particulate Tuscarora quartz using an aerosol suspension technique described previously by Davis et al. (37). In the initial data set, the regression on the experimental points yielded a slope of 463 counts cm^2 μg^{-1} with an intercept of 5.1 μg cm^{-2}. The limit of detection for quartz was found to be 0.6 μg cm^{-2} for particles collected on Teflon filters.

These studies have included a formal "variance error" analysis based on uncertainties known to exist or anticipated in the various measurements and physical parameters. In general, weight quantities are known to within 10% for major components in the sample. For minor components (i.e., less than 10% of the total mass) errors are quite variable, but may be as high as 100% or greater in some cases. The detection limit, or minimum amount detectable, is less than 1% for nearly all compounds.

Recently, Davis et al. (37) analyzed 104 pairs of Teflon filters collected in 1980 from 22 U.S. cities as part of the EPA's Inhalable Particulate Network (38). The filters were analyzed for elemental composition by EDXRF and for mineral content by an XRD procedure with the emphasis on the quartz content. Table 6A shows the elemental composition and quartz content of selected fine and coarse particles from four U.S. cities. Table 6B lists minerals that were observed to be present in almost all particle samples collected in the U.S. and their chemical composition.

From the analysis of these dichotomous filters from the 22 U.S. cities, it was noted that the continental interior sites showed the highest average ambient quartz concentration as well as the greatest variability. Coastal regions and eastern interior sites, with few exceptions, showed the lowest quartz concentrations in the ambient air. Perhaps the most notable exceptions

Table 6a. Elemental composition and quartz content of fine and coarse particles from three U.S. cities.

TYPICAL MASS-ELEMENTAL AND QUARTZ CONCENTRATION IN $\mu g/m^3$ AT SELECTED SITES IN THE UNITED STATES

	BOSTON, MASS		KANSAS CITY, MO		RIVERSIDE, CA	
	FINE	COARSE	FINE	COARSE	FINE	COARSE
MASS	34.9	105.9	25.7	44.7	35.2	71.0
AL	-	3.458	.091	2.053	0.036	3.513
SI	0.144	6.760	.434	4.542	.234	7.544
S	3.869	.502	1.816	.215	1.653	.720
Cl	-	.301	-	-	.009	.164
K	.096	.533	.311	.349	.120	.961
Ca	.070	1.069	.519	3.852	.301	4.781
V	.020	.008	-	-	.003	-
Fe	.121	1.612	.189	.800	.127	1.888
Ni	.012	.022	.002	.003	.007	.006
Cu	.035	.023	.032	.016	.040	.021
Zn	.046	.054	.034	.026	.029	.030
Br	.020	.025	.027	.009	.037	.028
Pb	.285	.177	.180	.057	.376	.113
QUARTZ	0	8.00	0	4.70	0	3.00

Table 6b. Minerals commonly found in ambient particles.

MINERALS COMMONLY PRESENT IN AMBIENT PARTICLES THAT CAN BE MEASURED BY X-RAY DIFFRACTION METHODOLOGY

MINERAL NAME	COMPOSITION
BIOTITE	$K_2MgFe_3(FeAl)Al_3Si_3)O_2 \cdot (OH)_3$
MUSCOVITE	$KAl_2(AlSi_3O_{10})(OH)_2$
GYPSUM	$CASO_4 \cdot 2H_2O$
KALONITE	$(Fe,al)_4\ Si_4O_{10}(OH)_8$
CALCITE	$CaCO_3$
PLAGIOCLASE	$0.55\ [NaAlSi_3O_8] + 0.45\ \ [CaAl_2Si_2O_8]$
DOLOMITE	$CaMg(CO_3)_2$
HEMATITE	Fe_2O_3
MAGNETITE	$FeO \cdot F_2O_3$
ANGLESITE	$PBSO_4$
MASCAGNITE	$[NH_4]_2SO_4$
THENARDITE	Na_2SO_4
SODANITER	$Na\ NO_3$
CHLORITE	NaCl

to this generalization are the sites of Inglenook and Tarrant, located in industrialized north Birmingham, AL, and El Paso, TX, where a quartz level was observed that was lower than expected for an arid inland site.

Comparison of these data with analyses made with polarizing OM by Bradway and Record (27) shows some interesting relationships. The filters studied by Bradway and Record were obtained from standard Hi-vol samplers of the National Aerometric Sampling Network (NASN), which did not have a wind insensitive sampling inlet. Therefore, the concentrations of quartz observed from these analyses should be considerably higher, in terms of weight percent of total suspended particulate (TSP), than those values obtained from the dichotomous sampler. Such is actually observed by comparison of the Bradway and Record (27) data with those of this paper. Three cities that were common to both the Bradway and Record (27) OM and the Davis et al. (37) XRD, OM particle classification studies were: North Birmingham, (Tarrand and Inglenook), St. Louis, MO, and Cincinnati, OH. In the Birmingham study, the Bradway and Record analyses showed 21 weight per cent quartz as an average of six filters, with the aerodynamic diameter particle size ranging from 5 to 60 μm with a median of about 15-μm diameter. This high level may be contrasted to the 4-7% observed in the dichotomous coarse fraction. Similarly, high values were observed by Bradway and Record in St. Louis (26 weight per cent for the 26-filter average, 6 sites). The presence of 40% calcite in the optical study agrees with our observation by XRD that calcite and dolomite constitute a significant fraction of the St. Louis filter mass. A similar result was obtained at Cincinnati where 19% quartz and 22% calcite was observed optically for the 20-filter average.

Quartz is often a major source of silicon in the coarse particle fraction of ambient aerosols. Feldspars, micas, and clays, however, contribute significant amounts of silicon in certain localities.

Davis' et al. (37) examination of the relationship between the silicon and quartz concentration for Buffalo, NY indicates that quartz was the major contributor of silicon, whereas less of a relative contribution from quartz was found in the samples from Birmingham and only very little was found from the Portland, OR site. Indeed, the examination of the XRD charts revealed that feldspars were the primary crustal component of the aerosols at Portland, OR, whereas at Buffalo only an occasional occurrence of feldspars and micas were observed; the other constituents were primarily carbonates and sulfates. This feature is also consistent with the higher Al and K contents of the Portland, OR sample.

DENUDER SAMPLERS

Nitrate and Nitric Acid Samples: Evidence is accumulating that indicates the importance of acidic nitrate in atmosphere deposition processes. For example, Lewis and Grant (39) have recently reported measurements of precipitation chemistry from a rural site in the Colorado Rockies and suggest that a decrease of nearly one pH unit over a period of four years was due to increasing nitric acid. The nature of nitrate deposition depends on the distribution of nitrates between gas and solid phases. A number of investigators (40), and (41) have recently made observations that indicate that, in both rural and urban atmospheres, gaseous nitrate concentrations are considerably larger than those of particulate nitrate. The contrasting behavior of atmospheric nitric acid (HNO_3) which appears in the gas phase, and sulfuric acid (H_2SO_4), which appears in particulate form, is consistent with their relative vapor pressures and heats of hydration.

The determination of background or rural values for nitrates is difficult; even at 10,000 ft in the Rocky Mountains, Kelley et al. (42) have

observed changes in HNO_3 concentrations of a factor of 100 depending on whether the wind was from the east or west. It is clear that techniques for measuring atmospheric nitrates should combine high sensitivity with unambiguous discrimination between gaseous and particulate nitrates.

As investigators have improved methods of sampling and analysis for atmospheric nitrate, it has become evident that the distribution of atmospheric nitrate between the gaseous and particulate phases has been masked by experimental artifacts. Many early particulate nitrate data were based on analyses of extracts from glass fiber aerosol filters used in Hi-vol samplers. It is now known that these filters contain active sites that fix gaseous HNO_3 and make it appear as particulate nitrate (43, 44). Other filter materials have also been shown to react with and collect gaseous HNO_3 and create a positive particulate nitrate artifact (45). The use of an inert filter material such as Teflon removes the "positive artifact" problem, except for the possibility of reaction with the collected aerosol particles. It has been shown, however, that collected aerosol nitrate particles (true particulate nitrate) may be lost from filters due to reactions with other materials or to evaporation. Loss of particulate nitrate is known as "negative artifact." Reactive loss may occur if, for example, H_2SO_4 aerosol comes in contact on the filter surface with nitrate aerosol. Evaporative loss may occur due to decreases in ambient gas concentrations causing the solid and gaseous nitrate phases to no longer be in equilibrium. Thus we see that, on the one hand, measurements of particulate nitrate using glass fiber filters are expected to be systematically high. If the recent measurements mentioned above of the distribution between HNO_3 and particulate nitrate are correct, the glass fiber filter nitrate overestimates may be considerable. On the other hand, measurements of particulate nitrate using inert Teflon filters are expected to

be systematically low, but the extent of loss due to reaction and evaporation are difficult to predict.

Given the free energy change of vaporization for NH_4NO_3, it is straightforward to calculate the vapor pressures of NH_3 and HNO_3 in equilibrium with NH_4NO_3 in the solid phase (46). These calculations show that at 10°C and 30°C the gas-phase equilibrium concentrations of both NH_3 and HNO_3 required to sustain the solid phase are ≅4 and 12 ppb, respectively. Tang (47) carried out considerably more detailed studies of the vapor pressures of HNO_3 and NH_3 in equilibrium with solution droplets of ammonium salts and has estimated the dependence of these vapor pressures on humidity and droplet acidity. Tang's work provides quantitative estimates of the increase of HNO_3 and decrease of HN_3 vapor pressures with increasing acidity and of the decrease of HNO_3 and NH_3 vapor pressures with increasing humidity.

Given the results of these calculations for estimating gas phase concentrations of HN_3 and HNO_3 required to support solid or solution phase nitrate and given the typical observed values of ambient NH_3 and HNO_3 concentrations, one may wonder why nitrates are ever observed in particles except in extraordinary circumstances. The components of the atmosphere, however, are generally not at thermodynamic equilibrium and the rate of approach to equilibrium between the solid and gas phase may be decreased by the intervention of other materials or phases. For example, the vapor pressure of water above a saturated solution of NH_4NO_3 is such that the solid phase is hygroscopic at relative humidites >60% over the temperature range 20-30°C. This means that at relative humidities exceeding 60% particles of NH_4NO_3 will accumulate an aqueous layer. As long as the solid phase is present, the equilibrium vapor pressures of NH_3 and HNO_3 will be unchanged, but the rate of approach to equilibrium will be retarded. Alternatively, a

particle may accumulate a layer of atmospheric organic material that would retard the loss of material from the solid to the gas phase. Because the nonpolar organic molecules will reduce the dielectric constant of the solution, it is energetically favorable for them to remain on the surface of the particle; hence, a skin may be formed. Chang and Hill (48) have shown that aqueous drop evaporation is retarded by the accumulation of gaseous mixtures of ozone and olefins and they provide references to earlier work on the reduction of evaporation by organic films. Apparently, losses of atmospheric particles due to evaporation are strongly dependent on other components in the atmosphere. It may be for these reasons that nitrate in aerosols is stabilized with respect to evaporation.

In order to avoid both positive and negative artifacts, a sampling system developed by Shaw et al. (49) has been tested and used in a number of EPA field studies on the system, termed the denuder difference method (DDM), is depicted in Figure 11a. Figure 11b is a photograph of a combined DDM and fine particle collection device to measure sulfate, fine particle mass, and SO_2. The experimental set-up for the DDM consists of Teflon cyclone to remove the coarse particles. The ambient air passes through the cyclone at ~ 30 L/min, and into a manifold where two parallel samples are collected at 3 L/min downstream of two tubes. One of the tubes, the denuder, is coated with MgO; the other tube, constructed of Teflon, is uncoated. The residence time of the gas and fine particles in the denuder is 0.2 s. After the air sample exits the tubes, it passes through a 25-mm diameter, 1-μm pore size Membrana nylon filter. The MgO removes the HNO_3 and the true fine particle nitrate is collected on the nylon filter. On the other nylon filter HNO_3 + fine particle nitrate is collected. The difference between the HNO_3 + nitrate sample and the fine nitrate is HNO_3, hence the name of the method.

The nylon filters are removed and stored in a sealed dessicator at 5°C until they are extracted. The nylon filters are extracted in 1×10^{-5} $NaHCO_3$ solution in an ultrasonic bath. The extract is analyzed by ion exchange chromatography for nitrate content. The precision of the method for 19 replicates is: nitrate = 0.1 $\mu g/m^3$, nitric acid = 0.2 $\mu g/m^3$. The precision refers to an ambient air sample size of 2.0 m^3. Figure 12 is a bar graph that compares measurements of gaseous nitrate and particle nitrate obtained using the DDM during the summer of 1980 in Research Triangle Park, NC.

RECEPTOR MODELING

Introduction: Once we have collected an ambient sample and determined the composition, the compositional data can be used in a model to help determine the sources of particles that impacted the monitoring (receptor) site. The modeling procedure that uses the aerosol composition measured at a receptor site is termed a receptor model.

It must be recognized at the beginning of this discussion that a receptor model, like all models, is a representation of reality. Scientists create models because they cannot effectively deal with all of the variables that affect the environment and because they want to see what the effects of changing some of those variables might be on others variables. Because some of the variables are always left out, a model is always an imperfect representation of the true situation. By improving models, scientists strive to decrease the difference between these representations and the real world. In both source-oriented and receptor-oriented environmental assessments, there are two representations of reality, the model and the measurements.

The receptor model is based on a scientific understanding of the interaction of matter and energy. It consists of a set of mathematical relationships between variables. This model, no matter how complex, is still

an inadequate representation of reality because no one can specify all of the important variables or the way in which they interact with each other. Values must be given to some of the variables that have been identified as important in order to determine their effects on the variables with unknown values. The selection of variables to which values are assigned and those for which values are calculated is what differentiates a source from a receptor model; the general physical model from which they are derived is the same.

Values are assigned to model variables through measurements, and measurements are also imperfect representations of reality. The specification of measurements includes: 1) the observables measured, 2) the range of values into which the measurements are confined, 3) the frequency and duration of measurements, 4) the spatial density of measurements, and 5) the validity, precision, and accuracy of the measurements.

Table 7 compares the number of significant physical variables and temporal and spatial scales for reality, measurements, source, and receptor models. These are only order-of-magnitude estimates, but reasonable changes could not reduce the vast difference between the number of variables for the real world and the number for any of the models and measurements.

Given this inability to even approach the conceptualization and measurement of so vast a number of variables, it might appear that there is no hope of ever coming to an understanding of what is happening in the atmosphere. However, if a full understanding cannot be reached, it can be approached by a careful interaction and refinement of models and measurements.

Fundamental to receptor modeling include these basic assumptions:

1. Composition of source emissions is constant.
2. Components do not react with each other if they add linearity.
3. p identified sources contribute to the receptor.

These assumptions lead to the following fundamental model. If a number of sources, p, exits and assumptions 1, 2, and 3 are valid, then the total airborne particulate mass measured at the receptor, C, will be a linear sum of the contributions of the individual sources S_j:

$$C = \sum_{j=1}^{p} S_j \qquad (2)$$

Similarly, the mass concentration of aerosol property i_j C_i, will be

$$C_i = \sum_{j=1}^{N} A_{ij} M_j \qquad (3)$$

Fractional abundance of element i in source component

Measured concentration of Element i

Deduced mass concentration for source component i

Where a_{ij} is the mass fraction of source contribution j possessing property i at the receptor.

When the property i is a chemical element (e.g., Pb), equation (3) represents a chemical mass balance. If one measures n chemical properties of both source emissions and particle composition at the receptor, n equations of the form of equation (3) exist. If the number of source types contributing to those properties is less than or equal to the number of equations, that is $p \leq n$, overdetermined system of linear equations.

Table 7. Comparisons of measurements and source and receptor model components with reality on an urban scale.

	Order of Magnitude Estimates			
	Reality	Measurement	Source Model	Receptor Model
Air Volume (m^3)	10^{11}[a]	10^3[b]	10^9[c]	10^3
No. of variables	10^3[d]	50	50	50
Range of pollutant concentrations (g)	10^{-15}--10^{-3}	10^{-9}--10^{-3}	10^{-6}--10^{-3}	10^{-9}--10^{-3}
No. of variable interactions	10^4[d]	100[e]	10	0
No. of pollutant sources	10^3	10	10^2	10
Range of pollutant emissions (g/sec)	10^{-2}--10^3	1--10^3	1--10^3	1--10^3
Emissions time scale resolution (sec)	10^2	10^7	10^7	10^7
Emissions spatial[f] scale resolution (m)	vert. 10 horz. 100	10 100	10 100	10 100
Dispersion time[g] scale resolution (sec)	10^2	10^2	10^3	10^4
Dispersion spatial scale resolution (m)	vert. 0--1000 horz. 100, micro 10^4, meso 10^6, macro	10, 100 1000 few few	10 1000 none none	10 1000 none none

[a]Volume of an urban area 10km x 10km with a 10^3m mixing height.

[b]Typical hi-vol sample volume.

[c]Gaussian plume models typically use wind data from 10m towers and calculate ground-level concentrations.

[d]Unknown: a rough estimate.

[e]This includes important chemical reactions.

[f]The precision with which emissions sources can be located.

[g]Time-scale of significant changes in wind speed and direction.

Receptor Modeling Study Example 1: Before a receptor modeling study is initiated, the elemental composition of aerosols collected within the airshed of interest should be carefully evaluated. If possible, ambient particles should be separated into fine (<2.5 μm) and coarse (>2.5 μm) fractions with dichotomous samplers over consecutive 12-h periods. These sampling periods should be adjusted so that daytime and nighttime samples can be obtained. For example, samples collected between 7:00 am and 7:00 pm (daytime) and 7:00 pm and 7:00 am (nighttime) during the winter are ideal for determining the impact of wood smoke on air quality.

Table 8 contains data on the aerosol composition of air samples collected by the U.S. EPA in Denver, CO, from January 19-20, 1982 and by Sandia Laboratories in Albuquerque, NM, from January 3-4, 1983. These two cities are very similar geographically in that they are both at elevations above 4,000 ft and are not highly industrialized. Neither city is affected substantially by coal-fired power plants, although within the Denver airshed there are several medium-sized power plants and an oil refinery. Dzubay et al. (50) report a relatively low average monthly aerosol sulfur concentration of 0.4 to 1.0 $\mu g/m^3$ for Dnver over a period of 1 year (1979), which implies that local and distant SO_2 sources are not the major contributors to visual air quality degradation. In contrast, Dzubay et al. (50) and Stevens et al. (22) have shown that in Houston, TX, and in the rural Shenandoah Valley fine sulfur particles were the principal contributors to the haziness in the summer.

In the limited study conducted by Sandia Laboratories in Albuquerque during the winter of 1983, ambient aerosol sulfur concentrations were similar to the low values observed in Denver during 1979 by Dzubay et al. (50). Both Denver and Albuquerque have what has been termed a wintertime "brown cloud" problem (see Figure 13). Ten years ago some scientists speculated that the

Table 8. Comparison of wintertime aerosol composition in Denver, CO and Albuquerque, NM.

	Denver, CO Jan. 19-20, 1982				Albuquerque, NM[a] Jan. 3-4, 1983			
	Night		Day		Night		Day	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Mass (μg/m³)	35.2	28.2	26.9	29.2	154.	16.0	41.0	37.0
Al	0.480	2.710	0.264	2.39	0.275	0.793	0.218	1.450
Si	0.413	6.900	0.247	6.16	0.070	2.14	0.138	3.790
S	1.050	0.230	1.54	0.245	0.737	0.162	0.932	0.293
Cl	0.056	0.636	0.045	1.01	0.165	0.193	0.31	0.948
K	0.118	0.575	0.061	0.510	0.611	0.263	0.113	0.423
Ca	0.059	0.583	0.051	0.531	0.062	0.843	0.780	1.530
V	BD[e]	BD	BD	BD	BD	BD	BD	BD
Mn	0.008	0.016	0.013	0.014	BD	0.008	BD	0.016
Fe	0.098	0.774	0.083	0.733	0.027	0.595	0.057	1.020
Ni	0.003	0.003	0.004	BD	BD	BD	BD	BD
Cu	0.018	0.009	0.012	BD	BD	0.004	0.000	0.005
Zn	0.043	0.020	0.029	0.017	0.039	0.032	0.027	0.055
As	BD	BD	BD	BD	BD	BD	BD	BD
Se	BD	BD	BD	BD	BD	BD	0.002	BD
Br	0.180	0.032	0.122	0.029	0.442	0.098	0.356	0.117
Pb	0.557	0.123	0.428	0.104	1.110	0.371	1.260	0.443
Sn	BD	BD	BD	BD	0.031	0.000	0.003	--
VC[b]	16.4	NM[c]	8.50	NM	75.0	5.0	15.0	2.0
EC[d]	3.23	NM	3.30	NM	15.0	2.0	5.0	1.0
Nitrate, total	3.40	NM	5.20	NM	9.11	NM	6.27	NM
Sulfate	2.62	0.352	4.64	0.366	2.27	0.84	2.51	1.33

[a] Air quality data collected by Sandia Laboratories (Dr. B. Zak, Principal Investigator) for the city of Albuquerque. This data set should be considered preliminary, since it is currently undergoing Department of Energy (DOE) quality assurance evaluation. The data were selected for this report to exemplify composition of fine particles in an airshed impacted by wood burning emissions. Data selected for periods when concentration of fine particle carbon at night $\gtrsim$ 20 μg/m³. Nitrate measured in Albuquerque is not total nitrate, but nitrate remaining in fine particle sample after collection.

[b] VC = volatile carbon.

[c] NM = not measured

[d] EC = elemental carbon.

[e] BD = below detection level

haze was caused by wind-blown dust. More recent wintertime studies by Wolff et al. (52) have shown that in Denver the haze results principally from fine particulates. In the studies by Wolff et al. (52) and by Lewis and Stevens (53) the brown cloud of Denver in the winter resulted mainly from carbon, sulfate, and nitrate, which are found in the fine fraction (<2.5 μm).

Because of the geographic and socio-economic similarity between the two cities, the data in Table 8 can be used to illustrate how a simple receptor modeling calculation from a few air samples can assist in determining the relative contributions of local emission sources on air quality. For example, in the case of the data set for Albuquerque we see that the nighttime potassium concentration in the fine particles was 5-times higher than that in the daytime period. Also, the total carbon concentration in the nighttime period was 4.5-times higher (90 $\mu g/m^3$) than in the daytime sample. On the other hand, the lead concentrations in the fine particles were approximately the same (~ 1.0 $\mu g/m^3$) for both the day and night samples and indicate, to a first approximation, that the carbon contribution from mobile vehicles was about the same for the two sampling periods.

From the studies performed by DeCesar and Cooper (54) and Stiles (55), we conclude potassium was approximately 1% of the fine particle emissions from pine wood burning. In Albuquerque most of the wood burned is a pine variety. (The ratio of potassium to fine particle emissions from wood burning of different types of wood is an area that requires considerably more research to establish emission rates for a variety of woods and to determine the range of uncertainty in these emission measurements. This will be discussed in more detail later in the text.) Since the potassium concentration at night in the fine particle sample was 0.61 $\mu g/m^3$, the total fine particle mass from wood burning that would accompany the potassium would be: $0.61 \div 0.01 = 61\ \mu g/m^3$.

This calculation assumes that all of the potassium in the fine fraction originates from wood burning, and the pathways for transport of the potassium and associated mass from wood burning are identical. Another assumption is that most wood burning occurs at night. We believe this assumption is reasonable, based on the habits of most individuals who use wood stoves or fireplaces and on the results obtained by a survey performed by Dennis (56). Thus, based on this simple calculation and these assumptions, 61 $\mu g/m^3$ of the 154 $\mu g/m^3$ is probably due to wood burning. About 80% of the fine particles from wood burning are in the form of carbon. Therefore, for this sampling period 52 $\mu g/m^3$ of the total carbon appears to be from wood burning. Multivariate analyses of the Albuquerque data set performed by Sandia Laboratories indicate the balance of the total carbon in this fine particles sample from Albuquerque appear to be from motor vehicles.

This crude calculation can be refined by using the elemental composition obtained from both the fine and coarse particles. In airsheds where coarse particles are likely to be abundant, it is essential that the potassium used as a tracer for wood burning be in the fine fraction and corrected for soil derived potassium. This is necessary because potassium is often abundant in the soil, and the amount of soil suspended as particles is dependent on meteorological conditions. During windy days, most of the soil particles are present in the coarse fraction, but some enrichment of the soil derived particles occurs in the fine fraction. For this reason, a correction for the potassium from the soil derived particles must be made to deduce the potassium from wood burning alone. This correction is described by Lewis and Stevens (53) and is based on the following equation:

$$K_{wood} = K_F - Fe_F \cdot (K_c/Fe_c)$$

where K_F = mass K in fine fraction,

Fe = mass Fe in fine fraction, (4)

K_c = mass K in coarse fraction, and

Fe_c = mass Fe in coarse fraction

In certain geographic areas, air quality measurements are not so clear as the observations made in Albuquerque. In those cases, a larger number of aerosol samples from ambient air and point sources may have to be collected to determine the contributions of sources to fine particles.

In contrast to Albuquerque, the analysis of the aerosols collected in January 1982 in Denver was considerably more complicated. The calculations were more complicated because the soil in Denver is rich in potassium, which makes the apportionment of carbon emissions from wood stoves using potassium, the tracer, dependent on knowledge of the soil compositions. In addition, the mass of fine particulates during the study never exceeded 42 $\mu g/m^3$, and the total carbon concentrations did not exceed 31 $\mu g/m^3$. These concentrations were substantially lower than those observed in Albuquerque. Therefore, in order to perform a viable source apportionment determination, the procedure of Kleinman et al. (57) was used to calculate the origins of the fine particulates. This receptor modeling procedure is based on an initial factor analysis of a set of elemental composition measurements from a minimum of 30 observations. With the single element tracers identified in this step, a multiple linear regression then determines the percentage impact of the sources associated with those tracers.

The results of this source apportionment calculation are shown in Table 9. Details of the source apportionment study performed in Denver are described by Lewis and Stevens (53)

Table 9. Denver source apportionment of wintertime fine particle composition (January 1982).

Sources Sources	Average Impact ($\mu g/m^3$)	Tracer Species[1]	%
Mobile Sources	9.2 ± 1.5	Pb	44
Power Plants	5.9 ± 1.1	$SO_4^=$	28
Crustal	1.7 ± 2.7	Si	8
Woodburning	1.3 ± 0.5	K[2]	6
Other (intercept)	2.7		13
Calculated	20.8		
Measured	20.1		

[1] Tracer species identified from factor analysis of data set.
[2] K concentration corrected for soil contribution to fine particle K.

Receptor Modeling Example 2: This receptor modeling exercise deals with a field study conducted jointly between the U.S. and the USSR in July of 1979. The experiment and results described below show how elemental composition, wind trajectory data, and SEM analysis of ambient particulate samples were used to determine the impact of a distant emission source on ambient air quality in what the USSR had termed a remote pristine site.

In an attempt to examine the properties of natural aerosol, investigators from the U.S. and USSR conducted the Abastumani Forest Aerosol Experiment (AFAEX-79) during July 1979 in the Georgian Republic of the USSR. The study site was at Abastumani Astrophysical Observatory, which is atop a conifer-covered mountain, 1650 m above mean sea level (MSL). The AFAEX-79 field measurements included concentrations of terpenes and their particulate oxidation products, meteorological conditions, gaseous species, aerosol size distributions, and optical coefficients (58, 59, 60).

For our contribution to AFAEX-79, we collected and analyzed ambient aerosol particles in three size ranges: ultrafine (<0.1 μm aerodynamic diameter), fine (<2.5 μm), and coarse (2.5-15 μm). A micro-orifice impactor

was used to remove particles larger than 0.1 μm (61) from the sampling air stream so that the ultrafine particles could be collected on a filter. Fine and coarse particles were collected in several dichotomous samplers equipped with Teflon, quartz, and Nuclepore filters and were analyzed for the species whose concentrations are shown in Table 10. Figure 14 shows time-series plots of sulfur and manganese concentrations in the fine fraction. Figure 14 also shows mean resultant wind vectors for the layer -- 1500 to 2100 m MSL. We computed these from rawinsonde ascents made three times daily (59).

Sulfate and ammonium accounted for 50% of the fine-fraction mass. X-ray fluorescence and ion exchange chromatography analyses together indicated within experimental error that all of the sulfur occurred as sulfate. No H^+ was detected, and sufficient NH_4^+ was measured to indicate that most of the sulfate occurred as ammonium sulfate, a conclusion that was confirmed by XRD analysis by Thompson et al. (62) of the fine particles. The amount of particulate carbon that Shaw et al. (60) could relate to terpene emissions was less than 4% of the fine-fraction mass. In the coarse fraction, montmorillonite, quartz, gypsum, and calcite were determined by XRD. Nitrate, a labile species, contributed 3.5% to the average coarse-fraction mass and may have been retained in the sample by reaction with the calcite. In general, the air we sampled was purer than that found in rural areas of the eastern U.S.A. (22). However, manganese appeared in unusually large concentrations in the fine and coarse particles.

To determine the nature of the particles containing manganese, the aerosols collected during the night of July 10 on 0.3-μm pore size Nuclepore filters were analyzed by SEM. Although most of the particles in the fine fraction contained only sulfate, spherical particles containing manganese and silicon and ranging in diameter from 0.5 to 1.5 μm were very prominant (Figure

15). The high manganese content and spherical shape of these particles indicate that they were emitted from a furnace or smelter. The mean resultant wind vectors indicate that air flowed to our sampling site from the north, where manganese mines at Chiatura and a manganese smelter at Zestafoni are located ~50 km from our sampling site. Manganese production at Chiatura and Zestafoni is second largest in the USSR. Isoentropic air parcel trajectories showed that the Abastumani air was not affected by emissions from the vicinity of Nikopol, 940 km to the northwest, where the USSR's largest manganese production occurs.

Particulate sulfur (Sp) concentrations measured in South America (63) are typically ~0.1 μg m^{-3} and represent an upper limit for the natural component from continental and oceanic sources. If the natural component of Sp in Europe is comparable to that in South America, then anthropogenic sources accounted for more than 90% of the 1.6 μg m^{-3} particulate sulfur at Abastumani. The major anthropogenic source of particulate sulfur is sulfur dioxide emissions that are transformed to sulfate in the atmosphere. According to an evaluation of emissions in Europe, SO_2 emissions in Georgia, where Abastumani is located, are among the lowest in Europe (64, 59) measured SO_2 at the study site and average value observed, expressed as sulfur in Table 10, was Sg = 0.05 μg m^{-3} and was among the lowest in Europe during July 1979 (65). The Sp/Sg ratio for Abastumani is 32 ± 6, much higher than for any of the other sites in Europe (65). Such a high Sp/Sg ratio indicates that the aerosol at Abastumani is well aged.

We can estimate the aging time for an ideal situation in which the SO_2 reaching our site is assumed to have originated from a single source and to have been transported via a single path. Use of an equation and rate constants by Trägardh (66) for this situation indicated that the aerosol reaching

Abastumani had aged for 147 ± 74 h. Three episodes of high sulfate concentrations at Abastumani were evaluated by isoentropic trajectory analysis. Two trajectories are shown in Figure 16. One episode could be explained in terms of rapid transport of an air parcel from Central Europe. For the other two episodes, the trajectories indicate four days of stagnation, which obscures the identity of any distant anthropogenic source of the sulfur reaching Abastumani.

Table 10. Average size fractionated aerosol composition (ng m^{-3}) at Abastumani Astrophysical Observatory between July 5 and July 24, 1979.

Species	Ultrafine	Fine	Coarse	Method	Filter
mass	250 ± 1400	12050 ± 3600	5350 ± 3100	β-gauge	Teflon
C_{or}		1710 ± 730	750 ± 660	pyrolysis	quartz
C_{el}		980 ± 150	108 ± 120	pyrolysis	quartz
H ion		<5	<5	titration	Teflon
ammonium		1390 ± 180	19 ± 23	electrochem.	Teflon
nitrate		<70	188 ± 22	IC	Teflon
sulfate		4600 ± 340	73 ± 85	IC	Teflon
Al	19 ± 31	98 ± 79	690 ± 270	XRF	Teflon
Si	11 ± 12	275 ± 36	1290 ± 430	XRF	Teflon
S	51 ± 6	1570 ± 115	81 ± 84	XRF	Teflon
Cl	0 ± 3	5 ± 7	28 ± 12	XRF	Teflon
K	9 ± 2	129 ± 10	100 ± 23	XRF	Teflon
Ca	2 ± 2	78 ± 7	327 ± 59	XRF	Teflon
Mn	3 ± 1	187 ± 14	38 ± 5	XRF	Teflon
Fe	2 ± 4	72 ± 10	196 ± 20	XRF	Teflon
Zn	2 ± 3	15 ± 7	6 ± 6	XRF	Teflon
Br	0.3 ± 0.1	3 ± 1	1 ± 1	XRF	Teflon
Pb	1.8 ± 0.5	18 ± 2	1 ± 1	XRF	Teflon

Conclusions

The major conclusions that can be drawn from this review of sampling and analytical methods to measure the composition of ambient particulate samples are as follows:

1. Collection of aerosols into two size ranges, fine and coarse fractions, simplifies the chemical analysis and preserves chemical integrity of acid species present in fine particles by removing the alkaline coarse particles before the particles are deposited onto the appropriate filter.

2. Two-micron pore size Teflon filters are recommended for particle collection when mass, elemental and ionic composition, and x-ray diffraction properties of the particles are to be measured.

3. Energy dispersive X-ray Fluorescence (XRF) Analysis and Neutron Activation Analysis are ideal analytical methods to measure the elemental composition of most of the elements present in ambient particles. XRF methods are preferred, because the analysis is completely non-destructive, highly sensitive, and can measure to within ± 10% such elements as Pb, Br, Cl, S, Cu, Si, Fe, Cu, K, As, Se and Cd at levels typically found in urban atmospheres.

4. Quartz filters are recommended when the carbon content of the particulate matter is to be measured. Combustion of the particulate samples at 650°C and 850°C differentiates the elemental or soot carbon from condensable organics present in ambient aerosols.

5. Nuclepore or esters of cellulose filter materials are typically used for SEM, TEM, or optical microscopic analysis of fine and coarse particles.

6. Sampling aerosols for microscopic or scanning electron microscopic analysis requires much shorter collection periods than for bulk elemental composition measurements.

7. Aerosol nitrate and nitric acid can only be reliably measured by use of HNO_3 denuders and nylon (or equivalent) filter materials.

8. Ion exchange chromatographic methods are recommended for the measurement of most anions and cations present in ambient particulate samples. If the appropriate precautions are followed, sulfites that may be if present in ambient particles can also be measured by ion chromatographic procedures.

9. X-ray diffraction can measure mineral content of particulate if the mass of particles per unit area on the filter is $\geq$ 200 μg/cm and soil standards from the airshed are available.

10. Major sources of particulate may be deduced from chemical composition of aerosol, additional analysis procedures, e.g. $^{14}C/^{12}C$, SEM, optical microscopic measurements, and meteorology will enhance the resolution of receptor models.

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Disclaimer:

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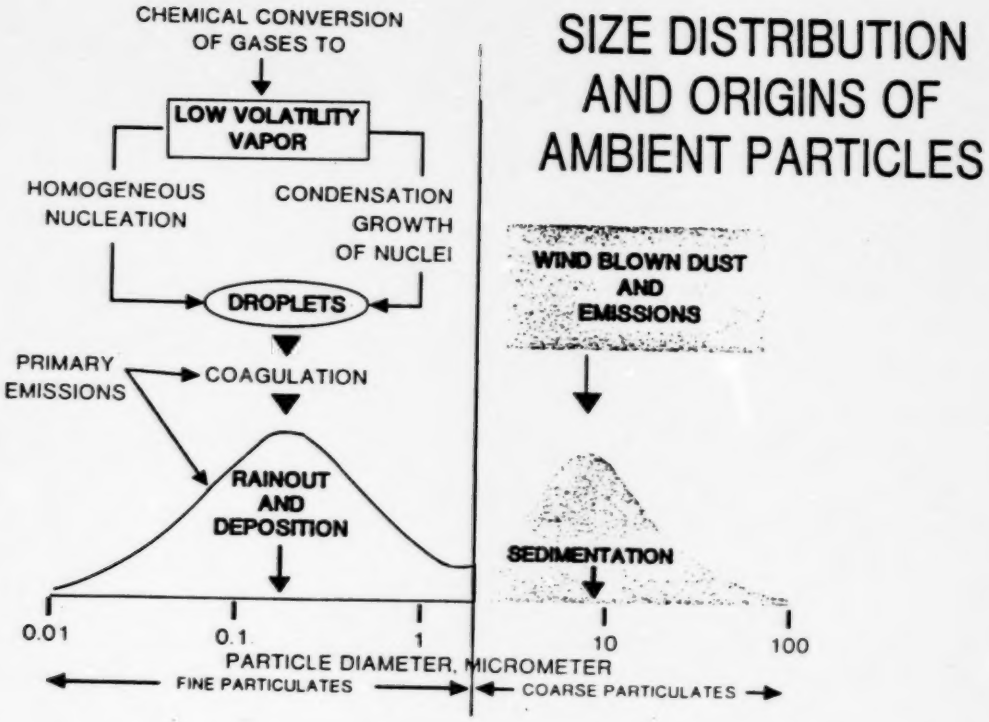

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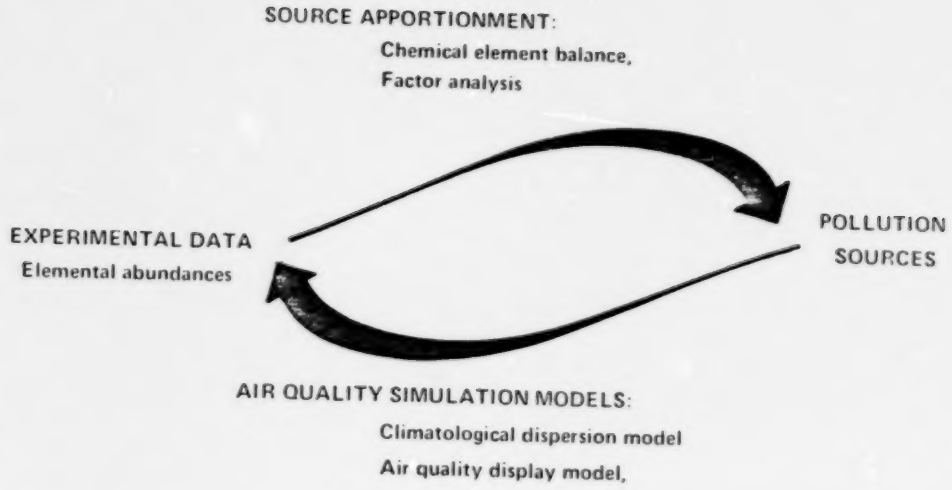

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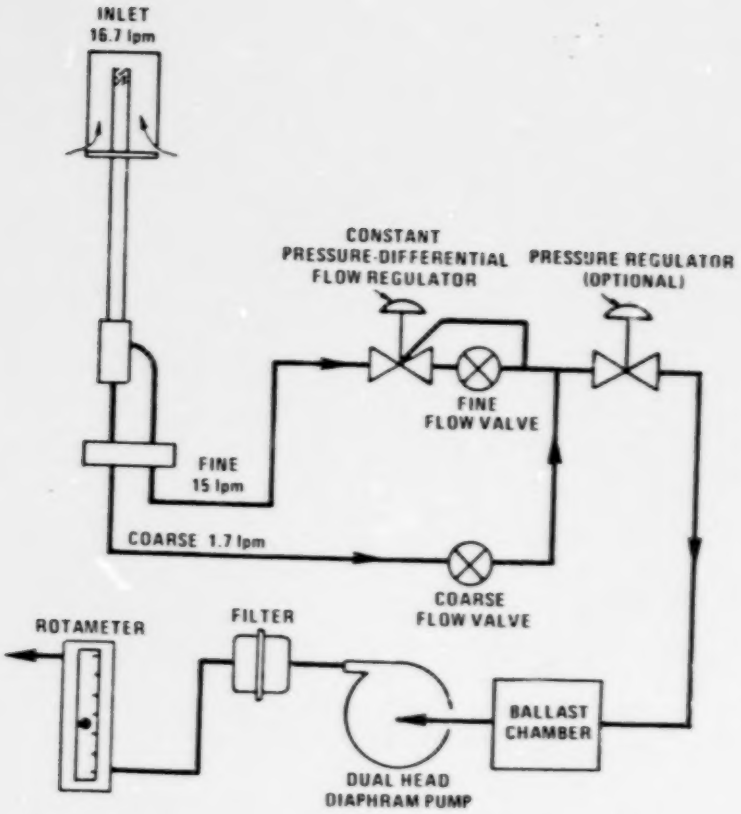

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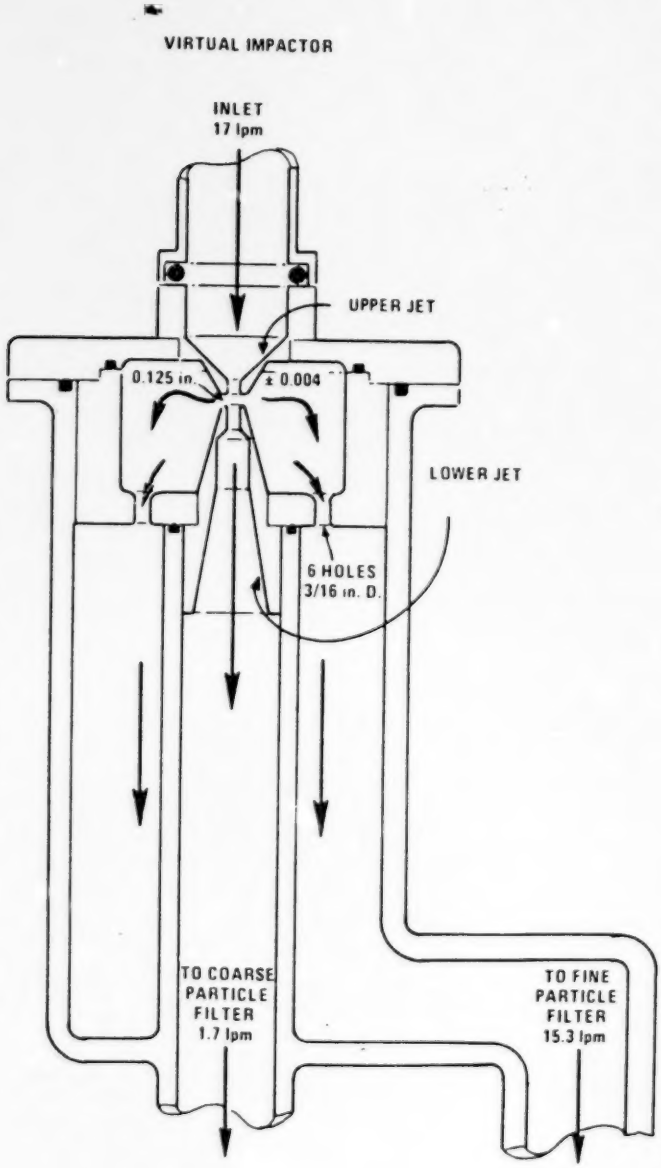
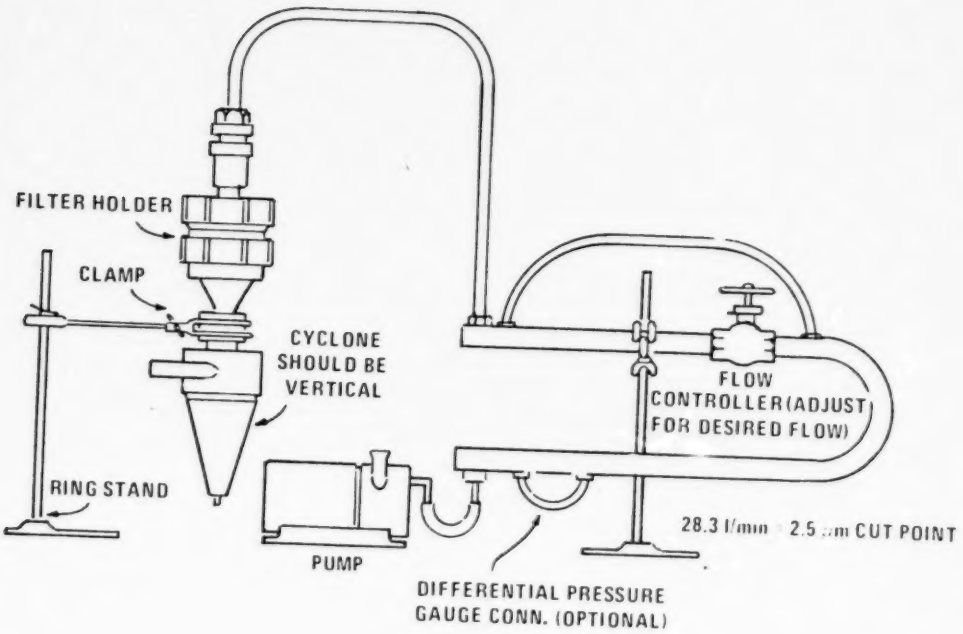


Figure 4. Diagram of Virtual Impactor



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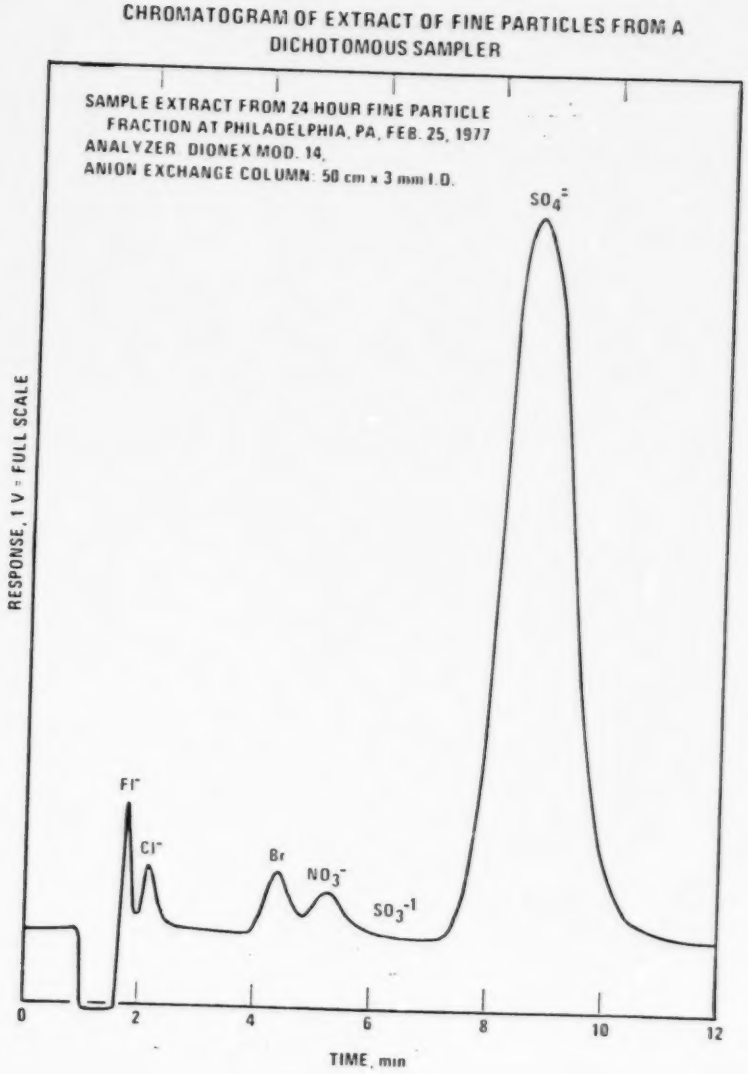

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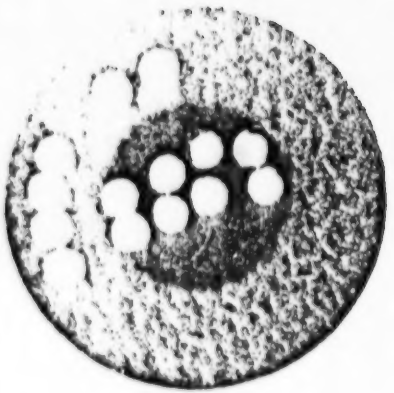
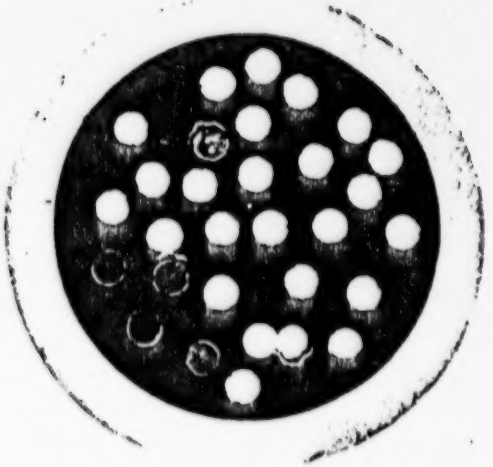
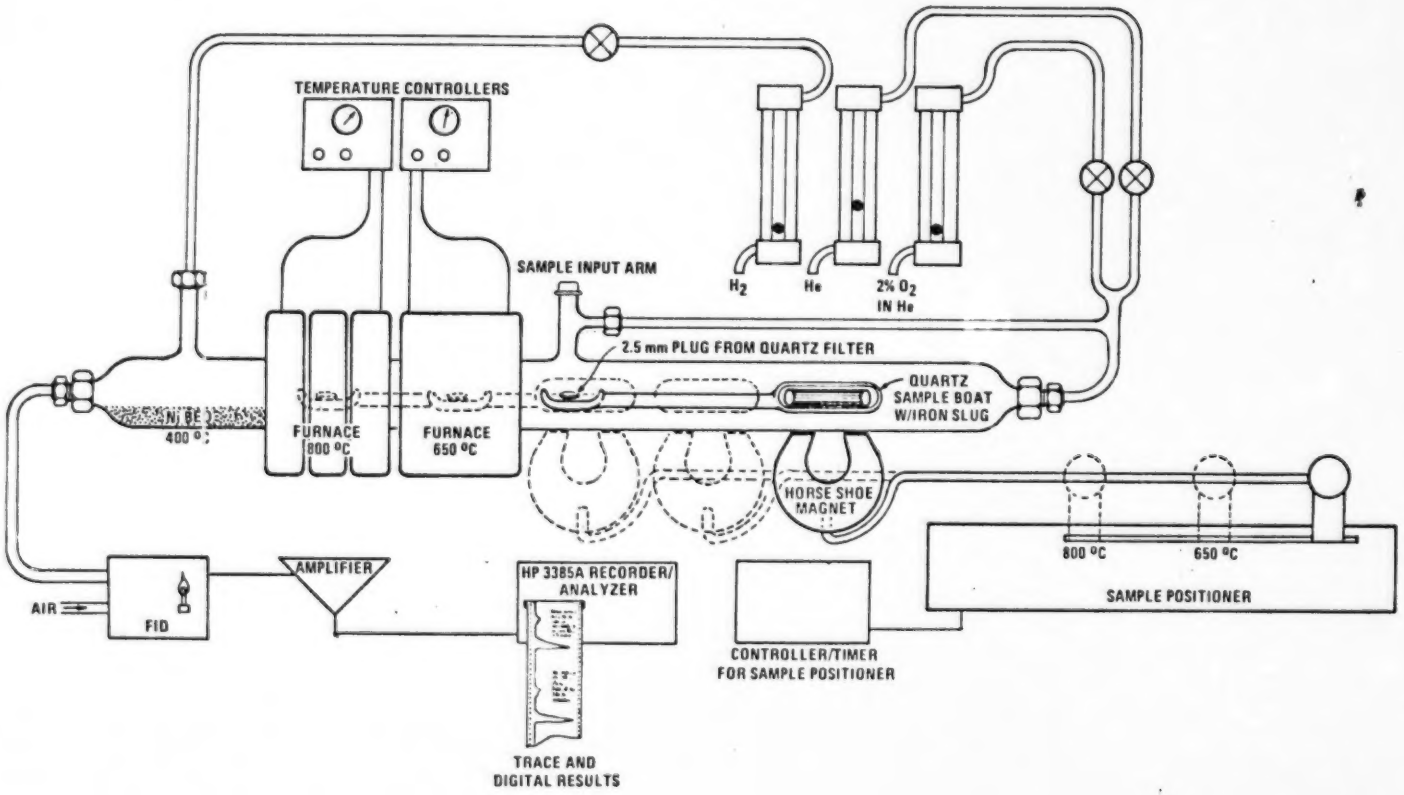


A



B

Figure 7. FINE PARTICLE SAMPLES COLLECTED ON QUARTZ FILTERS. SAMPLE A. COLLECTED BY MODIFYING SAMPLE FLOW TO FOCUS AEROSOLS INTO A 13 mm SPOT. THIS PROVIDES A HIGH DENSITY OF SAMPLE PER UNIT AREA AND REDUCES BLANK UNCERTAINTIES.
SAMPLE B. COLLECTED NORMALLY IN DENVER, CO, JAN., 1982 THE HOLES IN THE FILTERS ARE WHERE PIECES WERE REMOVED FOR CARBON ANALYSIS.



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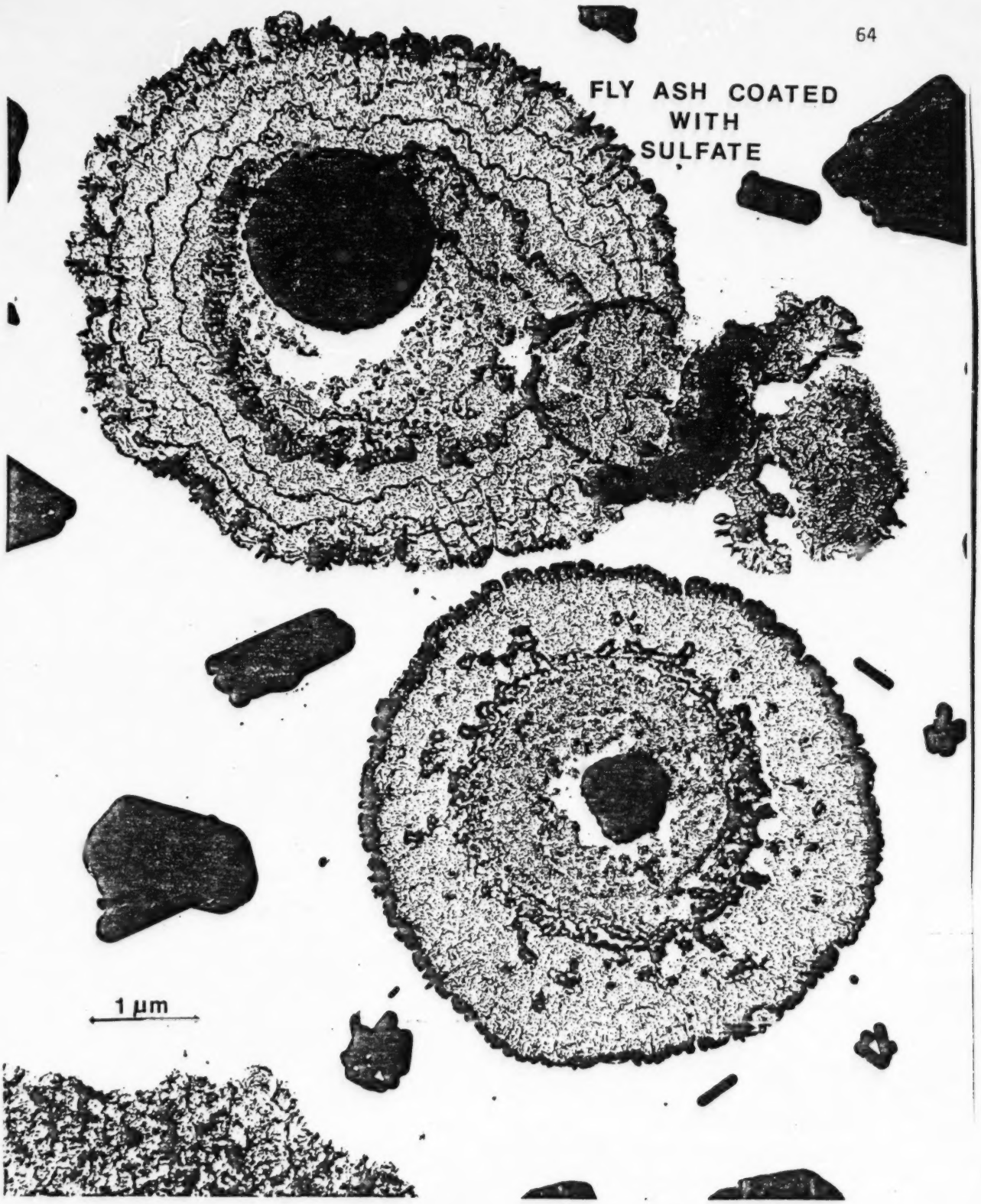

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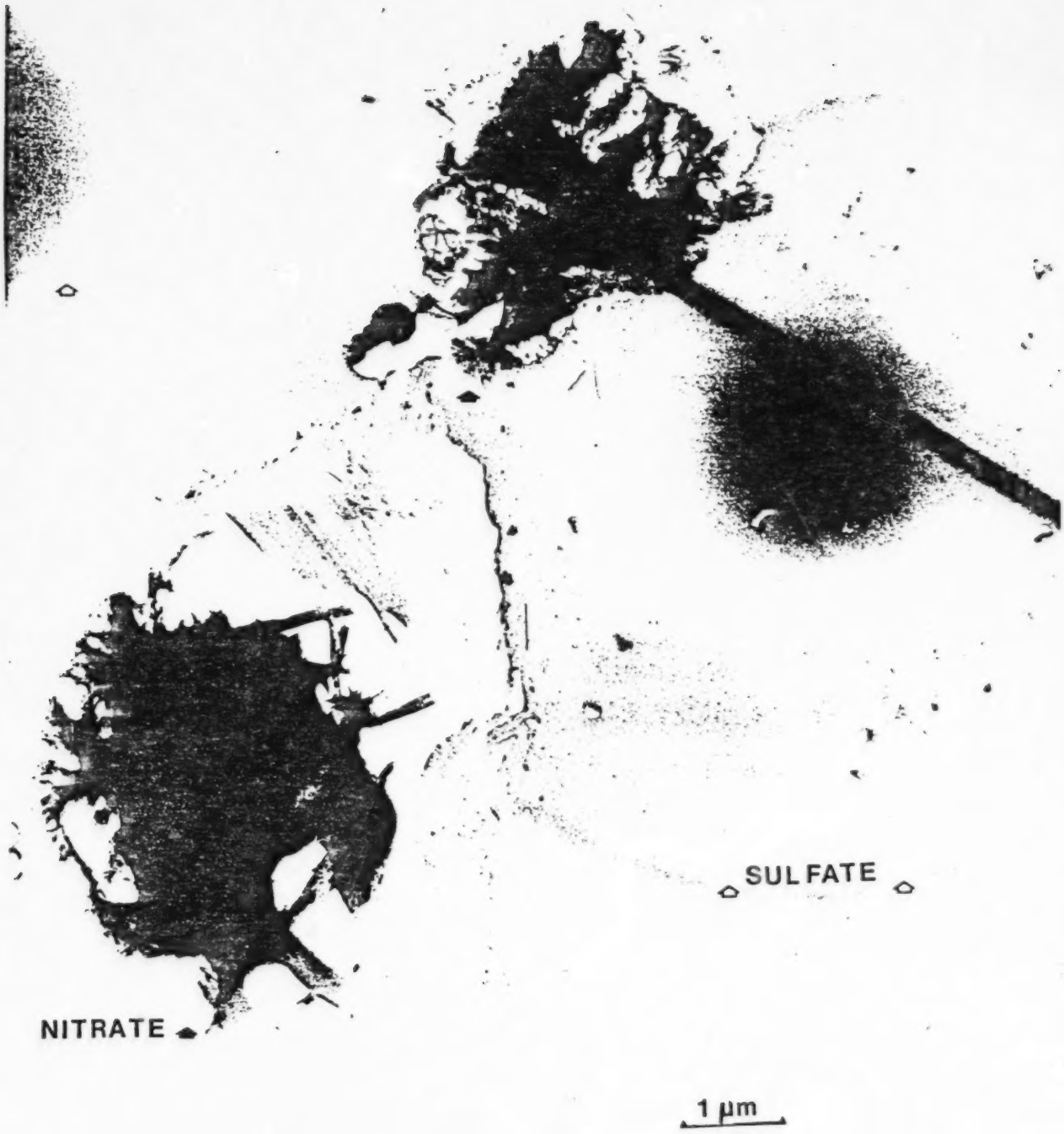

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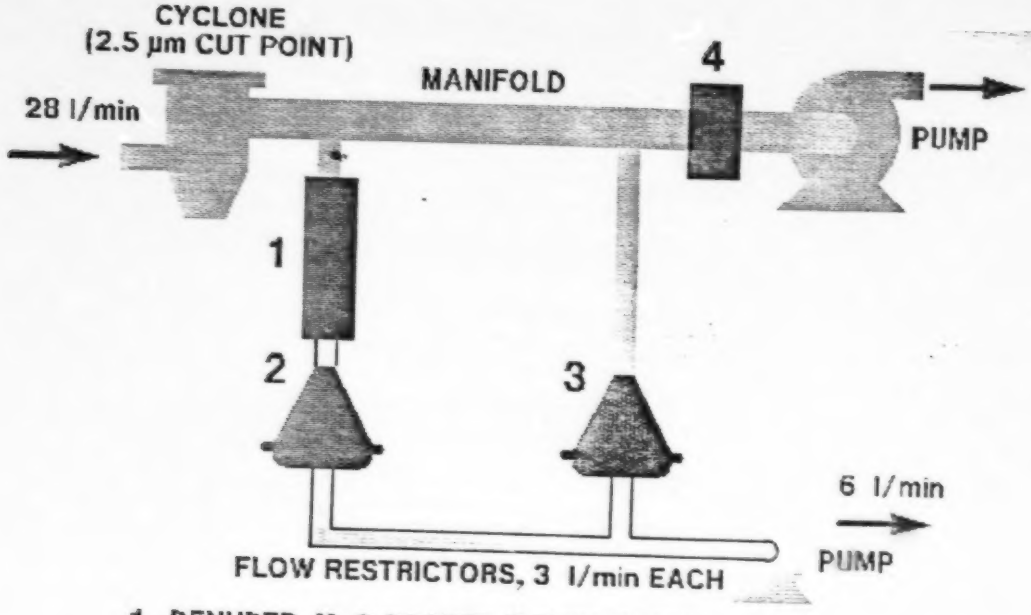


1. DENUDER, MgO COATED (REMOVES HNO_3)
2. FILTER, NYLON (COLLECTS NITRATE AEROSOLS)
3. FILTER, NYLON (COLLECTS HNO_3, NITRATES, AEROSOLS)
4. DIFFERENTIAL FLOW CONTROLLER

Figure 11a. Denuder difference method (DDM) sampler.

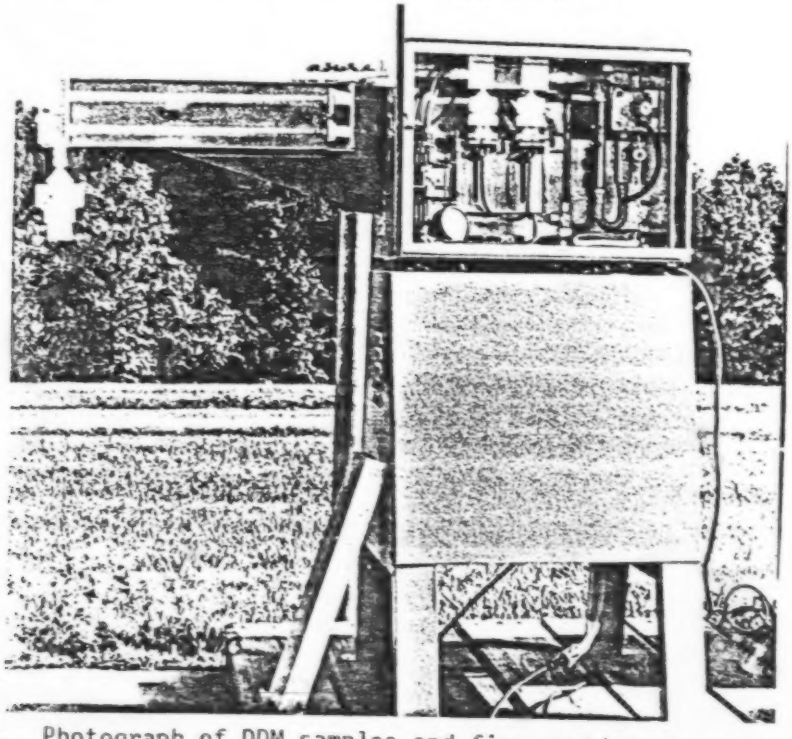
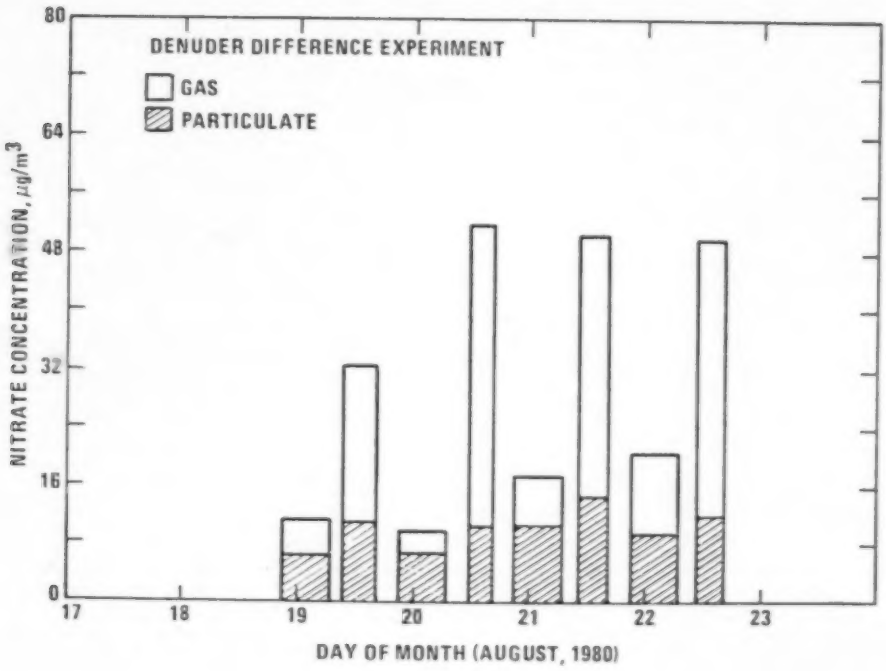


Figure 11b. Photograph of DDM samples and fine particle collector.



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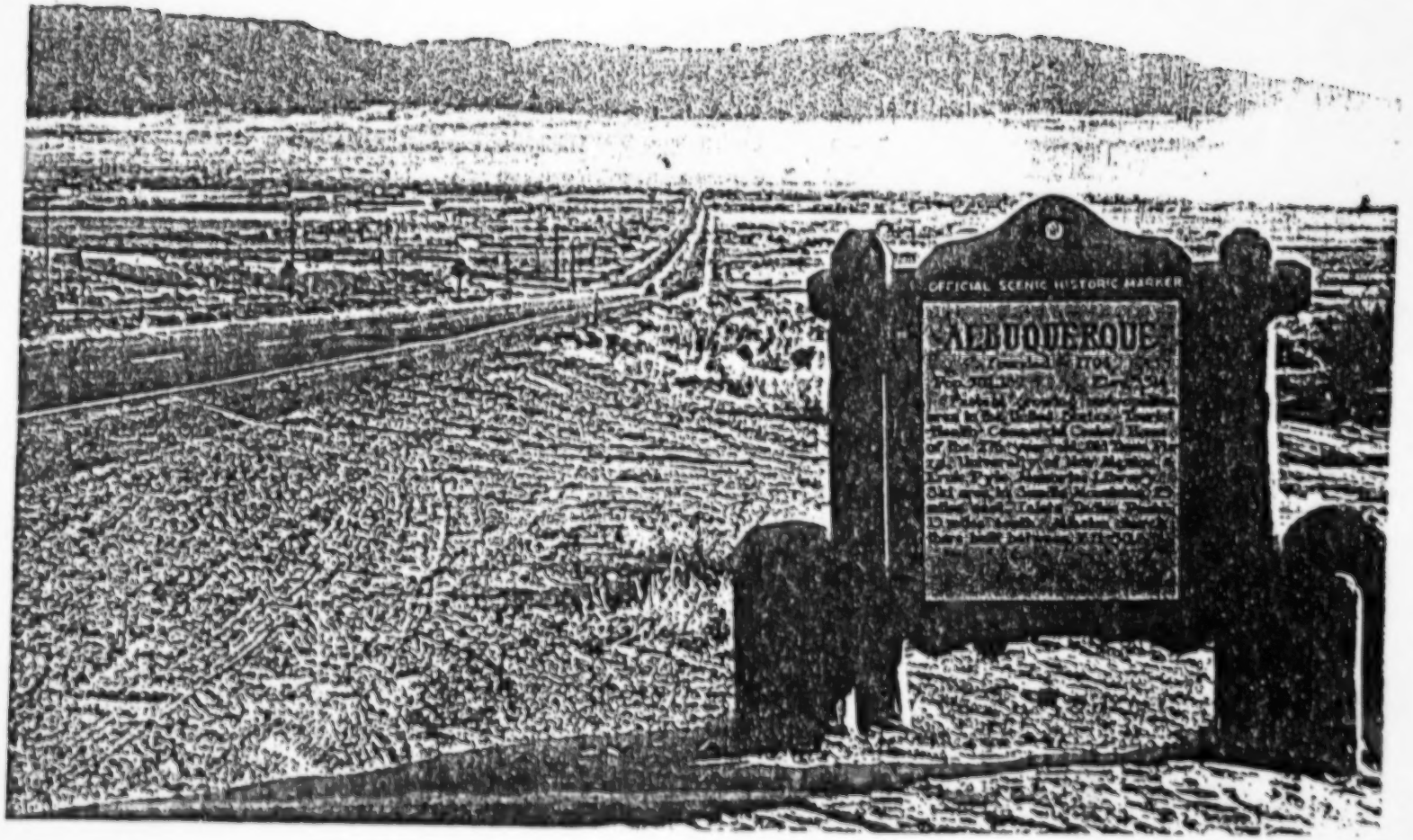

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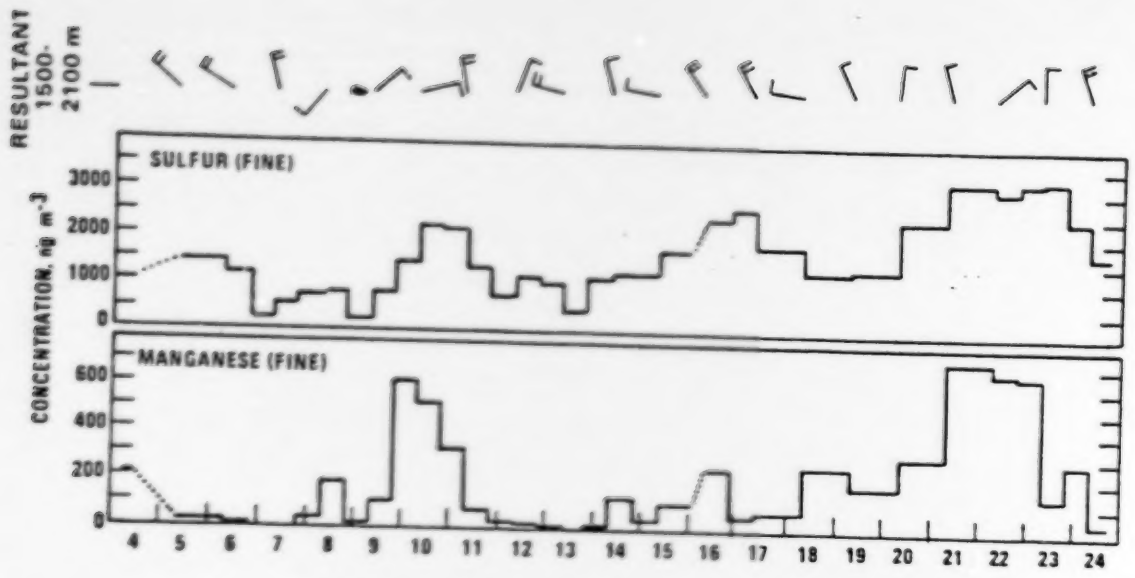

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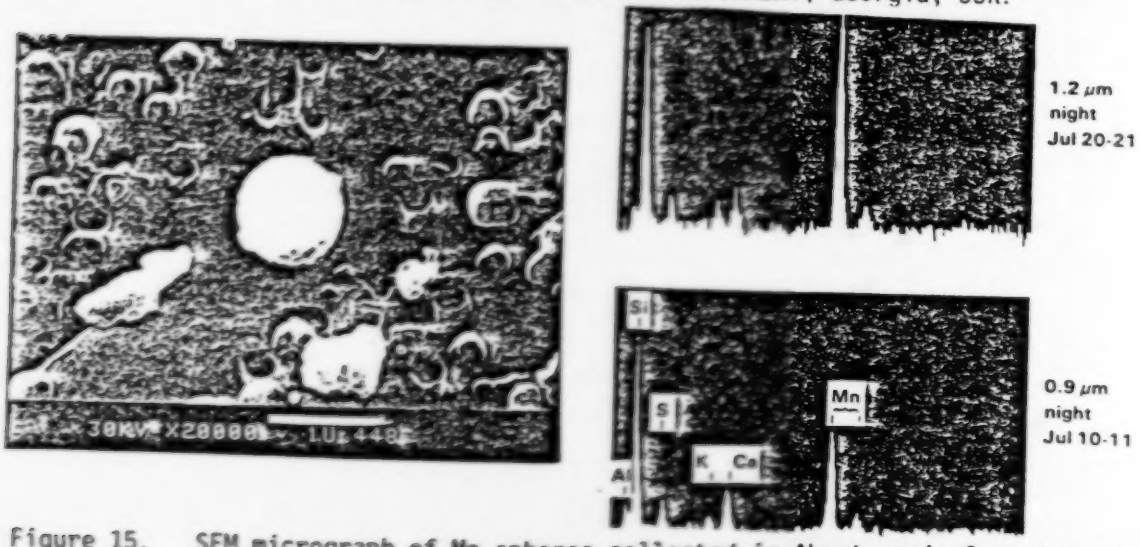

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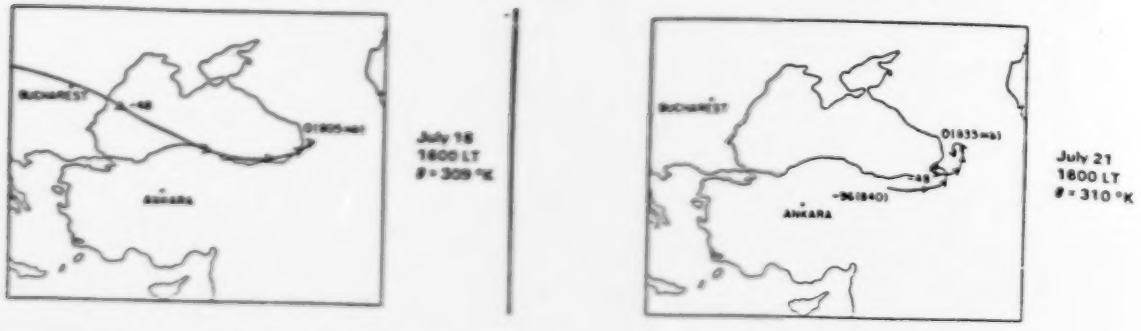

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